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HIGH INTENSITY LASER PROPAGATION IN THE ATMOSPHERE

FINAL REPORT

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HIGH INTENSITY LASER PROPAGATION IN THE ATMOSPHERE

Final Report

30 June 1969

Prepared by:

L. M. Frantz
L.M. Frantz
Theoretical Physics Department

T. D. Holstein
T.D. Holstein (Consultant)
(Permanent address:
Physics Department,
UCLA, California)

Approved by:

S. Altshuler
S. Altshuler (Project Manager)
Director
Quantum Physics Laboratory

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QUANTUM PHYSICS LABORATORY
Physical Research Center

TRW SYSTEMS
One Space Park
Redondo Beach, California 90278

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SUMMARY

FAR-WING COLLISION BROADENING STUDIES - Chapter I

The work reported in Chapter I is a continuation of our studies of absorption in the far wings of molecular bands. It is in these spectral regions that conventional pressure broadening theories of photo absorption are known to be inapplicable. A striking example is to be found in the far wings of certain infrared bands of CO_2. Here it is found that deviations from conventional (Lorentz-type) line shapes can assume order of magnitude proportions at spectral distances of the order of 100 to 200 cm^{-1} from the band center.

The present work is focused on the markedly sub-Lorentzian absorption which has been observed in the far wings of the CO_2 band centered at 2350 cm^{-1} (4.3 microns). The basic broadening mechanism is assumed to arise from perturbations of the rotational motion via short-range repulsive interaction between the absorbing molecule and a perturbing system (assumed monatomic for simplicity). In the limit in which the repulsive interaction is taken to have infinite slope (hard-sphere limit), the absorption is found to vary with frequency as $(\omega-\omega_0)^{-4}$. In the more realistic case in which the repulsive interaction is assumed to be of the form, $V = e^{-\alpha r}$ (with realistic values for the "range-constant," α), it is found that, in the far-wing, the absorption may be written as the product of a Lorentz line-shape and a factor which falls off exponentially with increasing frequency-shift from the line center, in general agreement with Benedict's empirical formula. In fact, an upper-bound estimate in the frequency range, $\omega-\omega_0$ = 200-250 cm^{-1}, is lower than the

measured absorption by a factor which varies from 10 to 15. It is strongly believed that this discrepancy is due principally to the omission of attractive interactions; their inclusion into the mathematical apparatus of the theory is feasible, and will constitute the subject matter of a future investigation.

BEAM DYNAMICS - Chapter II

We have obtained a fairly simple closed form expression for the maximum flux which the thermal self-defocusing effect permits us to transmit through the atmosphere. This analysis takes into account the effect of target motion, and is an extension of a previous analysis[1] in which only stationary targets are considered. In the case of a stationary target the limitation was found to be on the energy per unit area which can be transmitted, whereas for a moving target the limitation is found to be on the power density. The expression for the maximum flux depends upon such parameters as the initial beam intensity, the initial beam diameter, the target distance, the rotational rate of the beam and the effective absorption coefficient for heating of air by light at the laser frequency.

Our analysis is in the ray optics approximation, so that diffraction spreading is ignored. Furthermore, to avoid the complication of accounting for sonic effects, we have assumed that the time required for the beam to pass through any air mass is longer than the time required for sound to propagate in air across the beam; as a consequence, our results are meaningful only for targets moving at subsonic velocities. In addition, rather than

treat the rotation of the beam exactly by using time-varying initial conditions on the ray trajectories, we have simulated it by assigning to each air mass an effective illumination period, which depends on its distance from the laser.

In general the manner in which the beam self-defocuses depends upon the specific shape of its initial power profile. We have concerned ourselves with the special case in which the initial flux distribution is uniform in the interior of the beam, and falls off exponentially at the edge, as illustrated in Fig. 1. For this case we find that the interior rays propagate undeflected up to a certain distance, then deflect outwards; the closer the ray is to the edge, the shorter the distance is at which it first deflects (see Fig. 2). Therefore, the behavior of the beam may be described as follows: The flux in the interior remains undiminished, but the outer rays gradually peel off, so that the diameter of the undegraded interior decreases with distance.

Our solution is valid only in certain regions of space; as a result we cannot describe the behavior of the rays after they begin to deflect, but we can predict the diameter of the undegraded beam interior as a function of propagation distance. Therefore, as a criterion for when the beam has lost its effectiveness, we have assumed somewhat arbitrarily that the beam edge may be permitted to eat its way into the interior by no more than one fourth of the initial beam diameter.

Using this criterion we have provided several illustrative numerical examples; in all of these we have assumed a CO_2 laser with a diameter of

SUMMARY (continued)

one meter. For a stationary target in the zenith direction at an altitude much greater than the atmospheric scale height (8 km) we find a limiting energy/area of 0.95 joules/cm^2. For a stationary target on the ground at a distance of 1 km from the laser we find a limit of 240 joules/cm^2. If the target is flying directly overhead at an altitude of 10 km and with a velocity of 500 mph, we obtain a limiting flux of 197 watts/cm^2. Finally, if the target is on the ground and moving normal to the line of sight with a velocity of 10 m/sec (= 21.6 mph) at a distance of 1 km, we estimate a maximum flux of 610 watts/cm^2.

Chapter I

FAR-WING COLLISION BROADENING STUDIES

1. INTRODUCTION

In recent years, there has developed an awareness of the fact that published theories of pressure broadening of spectral lines are quite at variance with experiment with respect to magnitude and frequency-dependence of absorption in the extreme wings of the lines. In particular, in the case of infrared vibration-rotation molecular bands, the theories universally predict the Lorentz-line shape; their principal focus has to do with the dependence of the two parameters — width and shift — of the individual rotational components on such variables as J-values, temperature, and types of assumed intermolecular interactions. Experimentally, however, it is found that deviations from the Lorentz line-shape occur at spectral distances from the center of an individual line as small as a few cm^{-1}. In the extreme wings — at distances $\sim 100 - 200$ cm^{-1} from the band center of vibration-rotation lines — the discrepancies may assume order-of-magnitude proportions. In fact, recent experiments by Winters, Silverman, and Benedict[1] and Burch and Gryvnak[2] have shown that the absorption in the extreme high-frequency wings of a number of CO_2 bands is sub-Lorentzian by several orders of magnitude ($\gtrsim 10^{-2}$). Benedict et al[1] have in particular found that, in order to fit their experimental data, it was necessary to multiply the Lorentz shape by an empirical factor which decreases exponentially with increasing distance from the band-center. Similar results have been obtained by Burch and Gryvnak[2], with, however, one noteworthy exception. Namely, in the far-wing (high-frequency) wing of the $3\nu_3$-band of CO_2 in the vicinity of 7000 cm^{-1}, the absorption of the self-braodened band, while sub-Lorentzian, is much higher than that found by Benedict et al[1] for the comparable situation of the self-broadened wing of the fundamental ν_3 band (in the vicinity of 2400 cm^{-1}).

During the past year, work has been focused primarily on developing a basic understanding of the above described sub-Lorentzian behavior in the far wings of vibration-rotation bands. This work constitutes the subject matter of the present report.

Two basic mechanisms have been considered: (1) collisional perturbation of the rotational motion of the absorbing molecule, and (2) collisional perturbation of its vibrational motion. In our work, the main effort has been concentrated on the first of these, namely rotational perturbations.[3] The basic treatment is given in Section 2. Comparison with experiment (and discussion thereof) is presented in Section 3; in Section 4 future possible developments of the theory are outlined and overall prospects assessed.

With respect to the mechanism of vibrational perturbations, brief preliminary estimates, based on a simplification of the treatment given in one of our previous ONR reports[4] indicate that its contribution to the far-wing absorption is substantially smaller than that due to rotational perturbations. A systematic investigation of this mechanism is therefore reserved for the future.

2. ABSORPTION DUE TO ROTATIONAL PERTURBATIONS – BASIC THEORY

In this section, the far-wing absorption due to collisional perturbations of the rotational motion of a radiating molecule will be studied. In line with the remarks of the introduction, the radiating molecule will be taken to be a linear (CO_2-like) system; for simplicity the perturber will be assumed monatomic (noble-gas atom).

The starting point of the calculation is a vector generalization of equations (1) and (2) of a previous paper[5] for the spectral intensity, $I(\omega)$; it takes the form

$$I(\omega) = \left\langle |\underline{A}(\omega)|^2 \right\rangle_{Av} , \tag{2.1}$$

$$\underline{A}(\omega) = \frac{1}{(2\pi T)^{\frac{1}{2}}} \int_{-T/2}^{+T/2} e^{-i(\omega-\omega_0)t} \, \underline{n}(t)dt . \tag{2.2}$$

As in Ref. 5 the symbol $\langle \ldots \rangle_{Av}$ denotes an average over all types of collisions, and T is an arbitrarily large time interval. The new ingredient is the replacement of the scalar phase-shift factor, $e^{i\phi(t)}$, by the unit vector, $\underline{n}(t)$, giving the direction of the transition dipole-moment, $\underline{\mu}(t)$, of the radiating molecule via the expression,

$$\underline{\mu}(t) = \mu_0 \, \underline{n}(t) \, e^{i\omega_0 t} , \tag{2.3}$$

where μ_0 is the absolute magnitude of the transition dipole-moment[6] and where ω_0 is the frequency at the band origin, i.e., the frequency associated with purely vibrational motion. The time-variation of $\underline{n}(t)$ is thus associated solely with the rotatory motion of the axis of symmetry of the linear molecule;

in line with the experiments discussed in the introduction, the treatment will be confined to transitions involving the so-called ν_3-mode (i.e., asymmetric vibrations parallel to the axis of the linear molecule), so that $\underline{n}(t)$ is parallel to the axis of symmetry.

It may be remarked that, with $|\underline{n}(t)| = 1$, the factor $1/(2\pi T)^{\frac{1}{2}}$ in (2.2) guarantees that $I(\omega)$ is properly normalized, i.e.,

$$\int_0^{\infty} I(\omega)d\omega = 1 \quad . \tag{2.4}$$

In the present treatment, the rotational motion will be treated classically;[7] one then has

$$\frac{d\underline{n}(t)}{dt} = \underline{\omega}_p(t) \times \underline{n} \quad , \tag{2.5}$$

where $\omega_p(t)$ is the instantaneous rotational frequency.

Performing two successive integrations-by-parts, and introducing (2.5) one has

$$\underline{A}(\omega) = (2\pi T)^{-\frac{1}{2}} \int_{-T/2}^{+T/2} \frac{\underline{\omega}_p \times \underline{n}(t)}{i(\omega-\omega_0)} e^{-i(\omega-\omega_0)t} dt$$

$$\doteq (2\pi T)^{-\frac{1}{2}} \int_{-T/2}^{+T/2} \frac{\left\{\frac{d\underline{\omega}_p(t)}{dt} \times \underline{n}(t) + \underline{\omega}_p(t) \times \left[\underline{\omega}_p(t) \times \underline{n}(t)\right]\right\}}{-(\omega-\omega_0)^2} e^{-i(\omega-\omega_0)t} dt \; , \tag{2.6}$$

where the integrated terms at T/2 and -T/2 have been discarded.[8]

The basic motivation in going from (2.2) to (2.6) is contained in the classical picture of rotational perturbations, a picture originally developed by Debye, and which we feel particularly appropriate for the description of perturbations arising from short-range (repulsive) interaction potentials[9] between the radiating molecule and a (monatomic) perturber. According to this picture, the effect of such collisions is simply to change the vector angular velocity of rotation, $\underline{\omega}_p$ (generally, both in direction and magnitude). Following Debye, we shall assume (at least for the time being) that such changes occur instantaneously (impact-type collisions); subsequently, a generalization taking into account the finite time-duration of collisions will be introduced.

Accordingly, let it be assumed that the molecule undergoes a series of collisions at times $t_i(-T/2 < t_1 < t_2 < \ldots\ldots < t_i < \ldots\ldots < t_n < T/2)$, at which $\underline{\omega}_p$ changes suddenly. In particular, the angular velocities before and after the i'th collision are respectively denoted as $\underline{\omega}_{pi} - \Delta\underline{\omega}_i/2$ and $\underline{\omega}_{pi} + \Delta\underline{\omega}_i/2$; thus, $\Delta\underline{\omega}_i$ is the change at the i'th collision and $\underline{\omega}_{pi}$ is the arithmetic mean of the angular velocities before and after the i'th collision. It is then immediately apparent that, for the factor $d\underline{\omega}_p/dt$, occurring in the first term of the curly bracket of (2.6), one may write

$$\frac{d\underline{\omega}_p}{dt} = \sum_{i=1}^{N} \Delta\underline{\omega}_i \, \delta(t-t_i) \quad , \tag{2.7}$$

with the result that the contribution, $\underline{A}^{(1)}(\omega)$, of this first term to $\underline{A}(\omega)$ is

$$A^{(1)}(\omega) = -\sum_{i=1}^{N} (2\pi T)^{-\frac{1}{2}} \left[\frac{\Delta\underline{\omega}_i \times \underline{n}_i}{(\omega-\omega_0)^2}\right] e^{-i(\omega-\omega_0)t_i} \quad , \tag{2.8}$$

where $\underline{n}_i$ is the (momentary) orientation of the axis of the linear molecule at the time of the i'th impact, t_i.

In order to treat the second member of (2.6) in this spirit, let us carry out another integration-by-parts on it. Discarding, again, the physically spurious contributions at $\pm$ T/2, we have

$$\underline{A}(\omega)-\underline{A}^{(1)}(\omega) = (2\pi T)^{-\frac{1}{2}} \int_{-T/2}^{+T/2} \frac{\left\{\frac{d\underline{\omega}_p}{dt} \times \left[\omega_p \times \underline{n}(t)\right] + \underline{\omega}_p \times \left[\frac{d\underline{\omega}_p}{dt} \times \underline{n}(t)\right]\right\}}{i(\omega-\omega_0)^3} dt$$

$$+ \text{ Rem} \qquad (2.9)$$

where the term denoted as "Rem" is obtained by differentiating $\underline{n}(t)$ and using (2.5); its integrand is a vector-product expression involving the factor, $(\omega-\omega_0)^{-3}$, three powers of $\underline{\omega}_p(t)$, the orientation-vector $\underline{n}(t)$, and the exponential $e^{-i(\omega-\omega_0)t}$.

It is clear from these remarks that "Rem" may be treated by an additional integration-by-parts to yield terms whose integrands have magnitudes $\sim \frac{\omega_p^2 d\omega_p/dt}{(\omega-\omega_0)^4}$, together with "remainder-integrands" $\sim \omega_p^4/(\omega-\omega_0)^4$. Iterating this procedure, one may in fact construct a series in ascending powers of $\omega_p(t)/(\omega-\omega_0)$; it is here assumed without proof that such a series is at least <u>asymptotically</u> convergent (i.e., in that the error is of the order of the first discarded term). The applicability of the whole procedure then depends upon the smallness of the parameter, $\omega_p/(\omega-\omega_0)$, where ω_p is a typical rotational frequency. Assuming that this parameter is sufficiently small let us discard "Rem" in (2.9) without further ado.

The first term on the r.h.s. of (2.9), herewith designated as $\underline{A}^{(2)}(\omega)$, is now evaluated straightforwardly with the use of (2.7); one has

$$\underline{A}^{(2)}(\omega) = \sum_{i=1}^{N} (2\pi T)^{-\frac{1}{2}} \frac{\left\{\Delta\underline{\omega}_i \times \left[\underline{\omega}_{pi} \times \underline{n}_i\right] + \underline{\omega}_{pi} \times \left[\Delta\underline{\omega}_0 \times \underline{n}_i\right]\right\}}{i(\omega-\omega_0)^2} e^{-i(\omega-\omega_0)t_i} \quad . \tag{2.10}$$

Equation (2.10) is to be regarded as a first-order correction to $\underline{A}^{(1)}(\omega)$ in the (assumed) asymptotic series

$$\underline{A}(\omega) = \underline{A}^{(1)}(\omega) + \underline{A}^{(2)}(\omega) + \ldots. , \tag{2.11}$$

which has now to be inserted into (2.1).

In carrying out this last mentioned stage of the calculation, one may achieve a substantial simplification by introducing the so-called "wing-assumption," specifically, that

$$(\omega-\omega_0)\,\tau >> 1 \quad , \tag{2.12}$$

where τ is the mean time between successive collisions (assumed to be binary) This condition guarantees that the phase factors, $e^{-i(\omega-\omega_0)t_i}$ (after averaging over the appropriate statistical distribution of times between collisions, $t_{i+1} - t_i$, are essentially uncorrelated, i.e.,

$$\left\langle e^{-i(\omega-\omega_0)(t_j - t_i)} \right\rangle_{j\neq i} <<< 1 \quad . \tag{2.13}$$

Ignoring these correlations, it then follows (subject to one further qualification, to be discussed immediately below) that cross-terms in (2.1)(involving

products of contributions of <u>different</u> collisions) drop out, and one has

$$I(\omega) = \frac{1}{2\pi T} \sum_{i=1}^{N} \left| - \frac{\Delta\underline{\omega}_i \times \underline{n}_i}{(\omega-\omega_o)^2} + (\ldots\ldots)_i \right|^2_{Av} \qquad (2.14)$$

where $(\ldots\ldots)_i$ represents the i'th term in the r.h.s. of (2.10)[10].

The above mentioned qualification concerns the possibility that the orientation vector, $\underline{n}(t)$, may undergo variations between collisions which compensate those of the phase factor, $e^{i(\omega-\omega_o)t}$. It is however, immediately seen from (2.5) that this possibility can only be realized provided that there is available a rotational frequency, ω_p, in the near vicinity of $(\omega-\omega_o)$, such that

$$(\omega-\omega_o - \omega_p)\tau \sim 1 \quad .$$

But in this case our spectral frequency would be located close to one of the unperturbed rotational components of the band — a situation which is antithetical to that of interest in the present paper.

Returning to (2.14), one notes that, since the collisions are statistically independent of each other, the sum may simply be replaced by the total number of collisions in time T; since this number N is T/τ, one has

$$I(\omega) = \frac{1}{2\pi\tau} \left\langle \left| - \frac{\Delta\underline{\omega}_i \times \underline{n}_i}{(\omega-\omega_o)^2} + (\ldots\ldots)_i \right|^2 \right\rangle_{Av}$$

$$\simeq \frac{1}{2\pi\tau} \left\langle \left| \frac{\Delta\underline{\omega}_i \times \underline{n}_i}{(\omega-\omega_o)^2} \right|^2 \right\rangle_{Av} \qquad (2.15)$$

where the term $(.....)_i$ has been discarded in the interest of obtaining the simplest zero'th order result.[11] With $\Delta\omega_i$ perpendicular to $\underline{n}_i$ (as in the case for all angular velocities of rotation of linear molecules), (2.15) may be written as

$$I(\omega) = \frac{1}{2\pi\tau} \frac{\left\langle |\Delta\omega_i|^2 \right\rangle_{Av}}{(\omega-\omega_0)^4} \tag{2.16}$$

At this point, some brief remarks on the quantity, $1/\tau$, are in order. As remarked above (and as will be developed much more fully below), an impact-type approach is only valid when the duration, τ_c, of a collision is small compared to a time which (cf. especially (2.35) and (2.36) and the text paragraph after that containing these equations) is $\sim \frac{1}{|\omega-\omega_0|}$, i.e.,

$$|\omega-\omega_0|\tau_c << 1 \quad . \tag{2.17}$$

Now it turns out (as will be seen below) that for values of $|\omega-\omega_0|$ of experimental relevance ($\sim$ 200 cm^{-1}), (2.17) can be satisfied only for collisions governed by steeply rising, short-range repulsive potentials (in fact, rather more steeply rising than is realistically to be expected). Moreover, it will also be found that, when (2.17) is not satisfied, the predictions of impact theory, as given by (2.16), are modified principally by the inclusion of an exponential factor whose argument is $\sim 2\pi|\omega-\omega_0|\tau_c$.

From these remarks, it follows a fortiori that collisions of impact parameter appreciably larger than gas-kinetic radii — i.e., those involving the multipole-type, long range interactions (of predominant interest to the Lorentz-type impact theories,[12] whose domain of validity is confined

to the near vicinity of an individual rotational component of a band ($< 1\ cm^{-1}$) — will be quite ineffective in the far-wing region. Thus, in expressing $1/\tau$ in terms of a cross-section, σ , via the relationship

$$\frac{1}{\tau} = Nv\sigma \ , \tag{2.18}$$

(where v is a suitably averaged velocity of the perturbing atom relative to the radiating molecule), we must infer from the above remarks that σ is at most of the order of a gas-kinetic cross-section.

Excursus: At this point, it is of interest, and perhaps useful, to discuss certain other features of comparison between the Lorentz-type impact theories[12] and that contained in Eq. (2.16). As stated above (cf. Section 1), and explicitly in the cited references,[12] the Lorentz-type theories all predict line shapes whose wing-behavior is of the form

$$I(\omega) \propto \frac{1}{|\omega-\omega_0|^2} \ . \tag{2.19}$$

Now a fundamental postulate of these theories is that collisions be regarded as impacts — i.e., of time duration small compared to any other physically relevant time-like quantity in the problem. Our theory — or at least the version presented up to this point — is based on the same postulate. Nevertheless, as is clearly seen from (2.16), the frequency-dependence is of the type

$$I(\omega) \propto \frac{1}{|\omega-\omega_0|^4} \ .$$

Wherein lies the difference?

The answer, in our opinion, is contained in an additional assumption, first introduced implicitly by Anderson;[13] namely, if one is dealing with a number of lines (or individual components of a composite line) of frequencies $\omega_1 \ldots \omega_i \ldots$ it is necessary that the spectral frequency, ω, lie closer to any one of the lines, say ω_i, than to the others, i.e.,

$$|\omega-\omega_i| \ll |\omega-\omega_{j\neq i}| \quad . \tag{2.21}$$

In our theory, just the opposite assumption is made, namely[14]

$$|\omega-\omega_0| \gg |\Delta\underline{\omega}_i| \; .$$

It is hoped to verify the above conjecture in detail in the future. At this time we proceed to discuss matters rather more relevant for the interpretation of the CO_2 wing-experiments. Primary among these is the question of the validity of an impact-type theory (as described by Eq. (2.7) and the two paragraphs preceding it). Specifically, we now consider the effect of the actual time-duration of collisions — i.e., the time interval over which the collision-induced change in rotational frequency, $\Delta\omega_i$, occurs.

In order to investigate this question it is necessary to determine the details of the time variation of $\underline{\omega}_p(t)$ in the interval of collision.[15] To do this properly would involve rather complicated calculations and accurate knowledge of interatomic interactions (between the perturbing atom and those of the radiating linear molecule). Since the latter information is not available, and since we wish to get at the basic essence of the effect, we shall attack the problem in an admittedly simple-minded manner, as follows.

Let us begin by noting that, as remarked in the text surrounding Eq. (2.17), we have already restricted the treatment to a model in which the interaction V_{int}, between the radiating molecule and perturbing (noble-gas) atom is repulsive. In the interest of definiteness and simplicity, we now postulate a particular form for this interaction. Specifically, it is assumed that V_{int} is the <u>sum</u> of interactions between the noble-gas perturber and the individual atoms of the radiating molecule, i.e.,

$$V_{int} = \sum_i V_{ia} e^{-i\alpha_{ia}r_{ia}} , \qquad (2.23)$$

[where r_{ia} is the interatomic distance between the perturber (sympolized by subscript "a") and the i'th atomic constituent of the molecule, and the V_{ia} and α_{ia} are constants determining the magnitudes and ranges of the component interactions].

We have now to note a point of decisive importance for the calculation. Namely, the range constants, α_{ia}, turn out to be generally of the order of $4x10^8cm^{-1}$ (i.e., a few inverse angstroms), whereas a typical interaction distance, R_{ia}, defined, e.g. in terms of the distance of closest approach of two colliding atoms) is $\sim 3x10^{-8}$ i.e., a few angstroms; one thus has

$$\frac{1}{\alpha_{ia}R_{ia}} \sim \frac{1}{12} << 1 \quad . \qquad (2.24)$$

The smallness of the parameter, $1/\alpha_{ia}R_{ia}$, permits certain substantial simplifications. The most important of these is associated with the fact that the <u>depth of penetration</u> of two colliding atoms, which is $\sim 1/\alpha_{ia}$, and which, as will be seen shortly, is intimately linked up with the detailed

time-dependence of $\underline{\omega}_p$ in a collision interval, is small compared to the radius of curvature of surfaces of constant potential. This feature suggests that a reasonable approximation would be to neglect said curvature altogether. In particular, it suggests that the time-dependence of the relative velocity of the noble-gas atom with respect to its collision partner[16] (e.g., in the case of CO_2, one of the oxygen atoms) be treated as a one-dimensional problem of a particle moving in a potential field of the form $V\, e^{-\alpha x}$ (where the direction of the one-dimensional coordinate, x, is taken parallel to the line joining the centers of the two colliding atoms). For such a problem, it is immediately seen that only the normal component of relative velocity (parallel to the x-axis) would be altered by collision; denoting this component simply by v, one has

$$v = \frac{dx}{dt} = v_0\left[1 - e^{\alpha(x-x_c)}\right]^{-\frac{1}{2}} , \tag{2.25}$$

where x_c is the distance of closest approach,[17] and v_0 the normal component of relative velocity at infinity (i.e., outside the penetration region). The solution of (2.25) is

$$x = x_c + \frac{2}{\alpha} \log \cosh \frac{\alpha v_0(t-t_c)}{2} ,$$

which gives

$$v = v_0 \tanh \frac{\alpha v_0(t-t_0)}{2} , \tag{2.26}$$

(t_c being the time at which the distance of closest approach is attained).

Before proceeding further, we must point out that the relevance of the simple one-dimensional problem, discussed immediately above, to our problem rests upon an <u>additional approximation</u> in which the repulsive potential field is regarded as stationary (in the relative coordinate of the two atoms) during the time interval of a collision ($\sim 1/\alpha v_0$). Such an idealization would be valid provided that, apart from their interaction, the two colliding atoms could be considered as free, and hence moving in straight lines. Actually, however, one of the atoms is also rotating; taking this complication into account would require us to consider a problem in which the (planar) potential energy surface is undergoing rotatory motion. The neglect of such motion requires that the parameter $\omega_p/\alpha v_0$ be sufficiently small, i.e.,

$$\frac{\omega_p}{\alpha v_0} << 1 \quad . \tag{2.27}$$

It has now to be remarked that (2.27), which is equivalent to requiring that the angle of rotation during a collision interval be small (compared to a radian), may be somewhat more marginally satisfied in practice than (2.24). For example, in CO_2, $\omega_p = v_{rot}/R_{CO}$ where R_{CO} is the CO distance ($\sim$ 1 angstrom). In this case, (2.27) becomes

$$\frac{v_{rot}}{v_0}\,\frac{1}{\alpha R_{CO}} \gtrsim \frac{1}{4}\, v_{rot}/v_0 << 1 \quad .$$

Now, in the worst possible case, in which the noble-gas atom is very heavy, $v_{rot} \gtrsim v$ and one has $v_{rot}/v_0 \alpha R_{CO} \sim 1/4$, which is less satisfactory than (2.24).[18] However, in a treatment of the type given in this paper, it appears to us as

still appropriate to regard $\omega_p/\alpha v$ as a small parameter; higher order corrections can always be studied by perturbation techniques at some future occasion.[19]

Within the framework of conditions (2.24) and (2.27), we now postulate that the time-dependence of $\omega_p(t)$ in the interval of a collision is the same as that given by the r.h.s. of (2.26), i.e.,

$$\underline{\omega}_p(t) = \underline{\omega}_{pi} + \frac{\Delta\underline{\omega}_i}{2} \tanh \frac{\alpha v_i(t-t_i)}{2} \quad , \tag{2.28}$$

where v_i is the value of v_0 for the i'th collision.

The basis of this postulate is contained in the following physical argument. Let us consider, for example, the collision of a noble-gas atom with one of the oxygen atoms of a CO_2 molecule. Equation (2.26) implies that, during the collision-interval there exists a force, $\underline{F}$, given by

$$\underline{F} = \underline{F}_0 \operatorname{sech}^2\left[\frac{\alpha v_i(t-t_i)}{2}\right] \quad , \tag{2.29}$$

where [within the framework of (2.24) and (2.27)], $\underline{F}_0$ is a temporally-constant vector parallel to the line of centers of the two colliding atoms (at the time instant, t_i, of closest approach in the i'th collision). Now, the component of this force perpendicular to the CO_2 axis gives rise to a torque, which [again within the framework of (2.24) and (2.27)] is of the form

$$\underline{T} = \underline{T}_0 \operatorname{sech}^2 \frac{\alpha v_i(t-t_i)}{2} \tag{2.30a}$$

where

$$\underline{T}_0 = R_{CO}\, \underline{n} \times \underline{F}_0 \quad , \tag{2.30b}$$

(with $\underline{n}_i$ the value of $\underline{n}$ at $t = t_i$). Noting, now, that

$$I \frac{d\underline{\omega}_p}{dt} = \underline{T} \tag{2.31}$$

(with I = moment of inertia of the molecule), one integrates, obtaining (2.28)[20], q.e.d.

The stage has been reached where our program of going beyond the confines of impact theory may now be realized. Let us first obtain a lowest-order result by substituting (2.28) into the first term of (2.6). One has then to evaluate[21]

$$-\underline{A}_1(\omega) = (2\pi T)^{-\frac{1}{2}} \sum_i \int_{-T/2}^{+T/2} \frac{\alpha v_i(\Delta\underline{\omega}_i \times \underline{n}_i)}{4} \operatorname{sech}^2 \frac{\alpha v_i(t-t_i)}{2} e^{-i(\omega-\omega_0)t} dt. \tag{2.32}$$

Noting that the sech^2 factor in (2.32) limits the time integration to intervals, $\gtrsim 2/\alpha v_i$, which are small compared to the time between collisions, and that the phase factor $e^{i(\omega-\omega_0)t}$ undergoes many oscillations between collisions, one has

$$-\underline{A}_1(\omega) = (2\pi T)^{-\frac{1}{2}} \sum_i e^{-i(\omega-\omega_0)t_i} \Delta\underline{\omega}_i \times \underline{n}_i \mathcal{J}_i$$

where

$$\mathcal{J}_i = \frac{\alpha v_i}{4} \int_{-\infty}^{+\infty} \operatorname{sech}^2\left(\frac{\alpha v_i t}{2}\right) e^{-i(\omega-\omega_0)t} dt \quad , \tag{2.33}$$

is evaluated in Appendix I; the result [cf. (1.5)]

$$\mathscr{I}_i = \frac{2\pi(\omega-\omega_o)}{\alpha v_i} \frac{e^{-\pi(\omega-\omega_o)/\alpha v_i}}{1-e^{-2\pi(\omega-\omega_o)/\alpha v_i}} \quad . \tag{2.34}$$

The contribution of $\underline{A}_1(\omega)$ to $I(\omega)$ is obtained by the same procedure as was used earlier [cf. text between Eqs. (2.11) and (2.15)]; the result is

$$I(\omega) = \frac{1}{2\pi\tau} \left\langle \left| - \frac{\underline{\Delta\omega}_i \times \underline{n}_i}{(\omega-\omega_o)^2} \frac{2\pi(\omega-\omega_o)}{\alpha v_i} \frac{e^{-\pi(\omega-\omega_o)/\alpha v_i}}{1-e^{-2\pi(\omega-\omega_o)/\alpha v_i}} + (\ldots.)_i \right|^2 \right\rangle_{Av}$$

$$\cong \frac{1}{2\pi\tau} \left\langle \frac{|\Delta\omega_i|^2}{(\omega-\omega_o)^4} F\left(2\pi(\omega-\omega_o)/\alpha v_i\right) \right\rangle_{Av} \tag{2.35}$$

where

$$F(x) \equiv \frac{x^2 e^{-x}}{(1-e^{-x})^2} = \left(\frac{x/2}{\sinh x/2}\right)^2 , \tag{2.36}$$

(2.35) embodies two approximations. The first of these is the neglect of the term $(\ldots..)_i$ [which represents the contribution of the second term of (2.6)]. Unlike the impact case, discussed above, the smallness parameter is not ω_p/ω, but rather[22] $|\Delta\omega_p|\alpha v_i$; the second is based in the smallness of the parameter $\omega_{pi}/\alpha v_i$, in that in the first term of (2.6) $\underline{n}$ is taken to be constant [equal to its value, $\underline{n}_i$ at the instant of closest approach of the colliding atoms (cf. text surrounding (2.27) and following (2.28), especially footnote 19.

Equation (2.35), in conjunction with (2.36), contains the looked-for generalization of (2.15), i.e., the inclusion of the effect of the finite duration of collisions, $\tau_c \gtrsim 2/\alpha v_i$ (cf. Ref. 21). In particular, as $\tau_c \to 0$ [e.g., by going to the hard-sphere limit $\alpha \to \infty$, $F(2\pi(\omega-\omega_o)/\alpha v_i) \to 1$, and (2.35) reduces to (2.15)]. On the other hand, in the case that $|\omega-\omega_o|\tau_c$ is large, specifically, when

$$\frac{2\pi|\omega-\omega_o|}{\alpha v_i} \gg 1 \quad , \tag{2.37}$$

(the case which, as will be seen below, obtains in the far-wing experiments in CO_2), the "form-factor" $F(2\pi(\omega-\omega_o)/\alpha v_i)$ causes a sharp reduction in the spectral intensity, $I(\omega)$, [relative to the impact-theory expression (2.15)]. In particular, one has, to a sufficiently good approximation,

$$I(\omega) \cong \frac{1}{2\pi\tau(\omega-\omega_o)^2} \left\langle \frac{|\Delta\underline{\omega}_i|^2 4\pi^2}{\alpha^2 v_i^2} e^{-2\pi|\omega-\omega_o|/\alpha v_i} \right\rangle_{Av} \qquad (2.38$$

which begins to look like the empirical formula suggested by Benedict, et al.[1] However, in order to obtain an expression which can be compared with experiment, the rather complicated averaging process involving the consideration of all types of impacts (according to their initial trajectories) as well as a thermal average over all the velocities (those of translation of the colliding partners as well as that associated with the rotatory motion of the radiating molecule). The systematic treatment of the total averaging process

will be deferred for the future. However, certain preliminary studies, in particular those concerned with the thermal averaging of the relative velocity, v_i, [appearing in the exponential factor of (2.38)] will now be presented.[23]

The basis of the discussion is the fact that distribution of relative velocities, v_i, is given by the standard Boltzmann relation

$$P(v_i) = \frac{1}{\sqrt{2\pi v_T^2}} e^{-v_i^2/2v_T^2} , \qquad (2.39)$$

where v_T^2 is the mean square relative velocity.[24]

The normalization coefficient in (2.39) is chosen so as to include both signs of v_i. Since we are momentarily concerned with the collision of the perturber with a particular "surface-element" of the molecule (eventually to be averaged) we consider only positive v_i and therefore have

$$P(v_i) = \frac{2}{\sqrt{2\pi v_T^2}} e^{-v_i^2/2v_T^2} \qquad (2.39')$$

Inserting (2.39') into (2.38) one has

$$I(\omega) = \frac{1}{2\pi\tau(\omega-\omega_0)^2} \left\langle \int_0^\infty \frac{4\pi^2 |\Delta\underline{\omega}_i|^2}{\alpha^2 v^2} e^{-2\pi|\omega-\omega_0|/\alpha v} \times \frac{2}{(2\pi v_T^2)^{1/2}} e^{-v^2/2v_T^2} dv \right\rangle_{coll} , \qquad (2.40)$$

where $\langle\ldots\rangle_{coll}$ indicates that the average over the geometric variables defining collisions has yet to be taken. Looking now at the integral within the braces of (2.40), one notes that, under the condition specified by (2.37), the exponential factors in the integrand, which may collectively be written as $e^{-F(v)}$ where $F(v) \equiv 2\pi|\omega-\omega_0|/\alpha v + v^2/2v_T^2$, are sharply peaked about the value v_s at which $F(v)$ becomes a minimum. This circumstance suggests the use of the method of steepest descents, according to which $F(v)$ is approximated by the first two nonvanishing terms of its Taylor expansion about v_s, i.e.,

$$F(v) \cong F(v_s) + \frac{1}{2} F''(v_s)\,(v-v_s)^2$$

(the term linear in $(v-v_s)$ vanishing since v_s is determined by the condition that $F'(v_s) = 0$); moreover, the algebraic factors in the integrand, such as $\Delta\omega_i$ and v_i, are approximated by their values at the saddle point,[25] $\Delta\omega_s$ and v_s). Omitting the details of the calculation, one finds that

$$\text{(a)}\qquad v_s = v_T\left[\frac{2\pi|\omega-\omega_0|}{\alpha v_T}\right]^{-1/3}$$

$$\text{(b)}\qquad F(v_s) = \frac{3}{2}\left[\frac{2\pi|\omega-\omega_0|}{\alpha v_T}\right]^{-2/3}$$

$$\text{(c)}\qquad F''(v_s) = 3/v_T^2$$

so that

$$I(\omega) = \frac{1}{2\pi\tau(\omega-\omega_0)^2}\left\langle \frac{4\pi^2|\Delta\omega_s|^2}{\alpha^2 v_s^2}\left(\frac{4}{3}\right)^{1/2} e^{-\frac{3}{2}\left[\frac{2\pi|\omega-\omega_0|}{\alpha v_T}\right]^{2/3}}\right\rangle_{coll} \qquad (2.41)$$

It is now of interest to note that the ratio $|\Delta\omega_s|/v_s$, which appears in (2.41), is in fact uniquely determined by the atomic masses of the collision partners, the distance R_{CO}, and the geometrics of the collision. Namely, from footnote (20), one has, for any collision,

$$\Delta\omega = \frac{R_{CO}}{I} \underline{n} \times \int \underline{F} dt = \frac{R_{CO}}{I} (\underline{n} \times \underline{n}_c) \int |F| dt \quad , \qquad (2.42)$$

where $\underline{n}$ and $\underline{n}_c$ are unit vectors along the momentary molecular axis and the line-between-centers of the colliding atoms. On the other hand, $\int |F| dt$ is directly related to the relative velocity, v; in fact

$$\int |F| dt = 2Mv \qquad (2.43)$$

where M is the appropriate reduced mass[26] for the relative motion in the collision. Its calculation must be equivalent to that of v_T^2, by virtue of the fact that (2.39) must also be expressible as

$$\frac{1}{(2\pi v_T^2)^{1/2}} e^{-Mv^2/2kT} \quad ; \quad \text{i.e., } v_T^2 = kT/M \; .$$

An explicit expression for M is given in Appendix II (cf. text below).

Introducing, then, (2.42) and (2.43) into (2.41) one has

$$I(\omega) = \frac{1}{2\pi\tau|\omega-\omega_0|^2} \left\langle \frac{4\pi^2 M^2 \sin^2\theta}{\alpha^2 R_{CO}^2 M_0^2} \left(\frac{4}{3}\right)^{1/2} e^{-\frac{3}{2}\left[\frac{2\pi|\omega-\omega_0|}{\alpha v_T}\right]^{2/3}} \right\rangle_{coll} , \qquad (2.44)$$

where use has been made of the fact that $I_{CO_2} = 2R_{CO}^2 M_O$ (M_O = mass of oxygen atom); moreover, from Appendix II [Eqs. 2.24) and (2.25)], one has

$$v_T = (kT/M)^{1/2} \tag{2.45}$$

$$\frac{1}{M} = \left[\frac{1}{M_A} + \frac{1}{M_{CO_2}} + \frac{1}{2M_O}\sin^2\theta\right] , \tag{2.46}$$

where M_A, M_{CO_2}, and M_O are respectively the masses of the noble-gas perturber-atom, the CO_2 molecule, and an oxygen atom[27] and θ the angle between the molecular axis and the line-of-centers of colliding atoms ($\sin\theta = |\underline{n} \times \underline{n}_c|$).

3. COMPARISON WITH EXPERIMENT AND DISCUSSION

Let us begin by computing an upper bound for the magnitude of (2.44) at a frequency $\omega = 2600\ cm^{-1}$, such that $|\omega-\omega_0| = 250\ cm^{-1}$. This region corresponds to the maximum frequency attained in the cited experiments (cf. Ref. 1, Fig. 3, and Ref. 2, Fig. 14) on the fundamental ν_3 band of CO_2. The motivation for such a computation is our anticipation that the result will fall substantially below the experimental values. If this be the case, we shall regard the situation as promising, since we have not yet invoked attractive interactions; according to preliminary calculations these should give rise to an increase in absorption.[28]

It will be noted that, apart from the factor 2 occurring in its first denominator, (2.44) is the product of a Lorentzian line shape, multiplied by the quantity $\langle \ldots\ldots \rangle_{coll}$. Although, as has been remarked in Section 2 [cf. text subsequent to Eq. (2.16)], the factor $1/\tau$, occurring in (2.44), is expected to be substantially smaller than the corresponding quantities occurring in the standard Lorentz-type formulae (which apply to the near vicinities of individual rotational components), we shall ignore this difference for the time being. The main discrepancy between the Lorentz-type extrapolations used in the cited experiments (cf. Ref. 1, Fig. 2) and the experimental curves will therefore be sought in the factor, $\langle \ldots\ldots \rangle_{coll}$, of (2.44), which we now proceed to estimate.

For numerical values of the various quantities occurring in (2.44) (and in the subsidiary expressions (2.45) and (2.46) for v_T and M), we take

$$\alpha = 4 \times 10^{8}\ \text{cm}^{-1} \tag{3.1}$$

$$\omega-\omega_0 = 2\pi c(250) = (1.9 \times 10^{11})\ (250)\ \text{sec}^{-1} \tag{3.2}$$

$$kT = 300\ (1.38) \times 10^{-16} = 4.15 \times 10^{-14}\text{ergs} \tag{3.3}$$

$$M_A = 40\ M_H \tag{3.4}$$

$$M_{CO_2} = 44\ M_H \tag{3.5}$$

$$M_O = 16\ M_H \tag{3.6}$$

$$R_{CO} = 10^{-8}\ \text{cm}^{-1}\quad , \tag{3.7}$$

where $M_H = 1.67 \times 10^{-24}$ gm is the mass of the hydrogen atom. Utilizing (3.3, 4, 5, 6), one finds (upon setting $\sin\theta = 1$; it is shown below that this choice maximizes $\langle \ldots . \rangle_{coll}$)

$$M = 12.7\ M_H \tag{3.8}$$

$$v_T = 1.59 \times 10^{5}/(12.7)^{\frac{1}{2}} = 4.5 \times 10^{4}\ \text{cm/sec}\quad . \tag{3.9}$$

From these values, one has

$$\left(\frac{M}{M_O}\right)^2 = \left(\frac{12.7}{16}\right)^2 = .63 \tag{3.10}$$

$$\frac{3}{2}\left[\frac{2\pi|\omega-\omega_0|}{\alpha v_T}\right]^{2/3} = \tfrac{3}{2}(16.5)^{2/3} = 9.75 \tag{3.11}$$

so that

$$\begin{aligned}\langle \ldots . \rangle_{coll} &= (2.45)\ (.63)\ (4/3)^{\frac{1}{2}}\ e^{-9.75} \\ &= 1.78\ e^{-9.75} = (1.78)\ (.58 \times 10^{-4}) = 1.03 \times 10^{-4}\ .\end{aligned} \tag{3.12}$$

Let us now note that setting $\sin\theta = 1$ minimizes M, thereby maximizing v_T; the result is the maximization of the exponential factor in (2.44). The remaining $\sin\theta$-dependence, contained in the pre-exponential factor, may be written as the square of

$$\frac{M\sin}{M_0} = \frac{\sin\theta}{M_0/M_A + M_0/M_{CO_2} + (1/2)\sin^2\theta}$$

$$= \frac{\sin\theta}{.764 + .5\sin^2\theta} \tag{3.13}$$

which is easily shown to be a monotonically-increasing function of $\sin\theta$ in the range $0 \leq \sin\theta \leq 1$. Thus $\langle \ldots . \rangle_{coll}$ is maximized by taking $\sin\theta$ equal to unity, q.e.d.

To proceed further, we may take the liberty of using for $1/\tau$ a value equal to that quoted by Benedict et al (cf. reference 1, page 536) for CO_2- CO_2 collisions, namely one corresponding to a width parameter $\gamma = 1/2\pi c\tau$, of .094 cm^{-1} (at one atmosphere, STP; this condition is used herein and in what follows for all density-dependent quantities. Such a value for $1/\tau$ is quite maximal, first of all because of the remarks in the second paragraph of this section, and also because the γ for self-broadening is known to exceed that for foreign-gas broadening by a factor ~ 1.5 (cf. reference 1, page 536; also reference 2, Table III).

The absorption coefficient, $k(\omega)$, is given by the expression

$$k(\omega) = SI(\omega) \quad , \tag{3.14}$$

where S is the total line strength; its value for the fundamental ν_3 band of CO_2 (as given by reference 1, bottom of page 535) is

$$S = 2700 \text{ cm}^{-1} \text{ atm}^{-1}.$$

Substituting (2.44) into (3.14), one has[29]

$$k(\omega) = \frac{S}{2\pi\tau(\omega-\omega_0)^2} \left\langle \cdots \right\rangle_{coll}$$

$$\rightarrow \frac{(2700)(.094)}{2\pi(250)^2} \; 1.03 \times 10^{-4}$$

$$= .65 \times 10^{-2} \; (1.02 \times 10^{-4}) \; = \; .67 \times 10^{-7} \text{cm}^{-1} \text{ atm}^{-2} ,$$

which is lower than the value given by Burch's measurement for argon (cf. reference 2, Fig. 10) by a factor[30] $\gtrsim$ 15. In view of all the maximal estimates involved in the above calculation, it seems apparent that a new physical ingredient has to be introduced into the theory.[31]

However, as remarked in the first paragraph, such an ingredient already impends: namely, the existence of attractive interactions, especially the rapidly varying ones, such as the dispersion (van-der-Waals) interactions $\propto r^{-6}$, which attain considerable magnitudes at the distance of closest approach. Preliminary exploration indicates that these interactions can be incorporated into the mathematical apparatus of the theory. It would therefore be highly desirable (and is in fact intended) to pursue this direction in the near future.

4. FUTURE DEVELOPMENTS AND PROSPECTS

The concluding remarks of the preceding section have brought us to the stage where a discussion of further developments and overall prospects is now in order.

A. Further Developments of the Present Theory

1. As pointed out in the last section, the most urgent requirement is the introduction of attractive interactions; it is expected (cf. footnote 31) the effect of these would be to shorten τ_c and, hence, to increase the magnitude, while decreasing the slope, of $I(\omega)$ in the far wing.

2. A point of more theoretical (interpretative) interest is the feature, noted in the excursus following Eq. (2.20) of Section 2, that the frequency-dependence of our impact result for $I(\omega)\left(\propto 1/(\omega-\omega_0)^4\right)$ differs from the Lorentz-type variation $\left(\propto 1/(\omega-\omega_0)^2\right)$, usually exhibited by impact-type theories.[13] A tentative explanation was suggested in the text subsequent to Eq. (2.20). It remains to verify this suggestion by a detailed analysis; from it we may hope to achieve a deeper physical understanding of the standard Lorentz-type theories, based on the cited references.[13]

3. The preliminary estimates of the smallness of $I_{vib}(\omega)$ [which denotes the contribution of vibrational perturbations to $I(\omega)$], mentioned at the end of the Introduction, should be reinforced by a detailed, systematic investigation. In particular, it will be desirable to alter the treatment of reference 4 (which is for the case of a diatomic molecule) to apply to the somewhat more complicated situation of a linear triatomic molecule, such as CO_2.

4. Since the maximum values of $\hbar(\omega-\omega_0)$, encountered experimentally, are not really small compared to kT, quantum modifications of our treatment

should be considered. In this connection, it may be remarked that the treatment of $I_{vib}(\omega)$ given in reference 4 is quantum-mechanical, permitting a comparative study [for arbitrary $\hbar(\omega-\omega_0)$] with the classical limit [attained when $\hbar(\omega-\omega_0) \ll kT$]. It is proposed to carry out such a study; if it shows that quantum modifications are important under experimental conditions, an attempt to introduce them into the present theory should be made.

It must however be stated that, even with all the above-proposed improvements — including, of course, the proper evaluation of $1/\tau$ and $\langle \cdots \rangle_{coll}$ — i.e., a proper averaging over the geometrics of collisions (in place of the upper-bound estimates given in Section 3), the theory will still contain residual uncertainties, associated with those of intermolecular force laws; such uncertainties are augmented in $I(\omega)$, due to the exponential dependence of this quantity on interaction parameters (as shown, e.g., by (2.41); preliminary indications are that the introduction of attractive interactions will not affect this feature). Looking at the situation positively, however, one may utilize the present theory [augmented, of course, by the proposed extensions and improvements (especially the introduction of attractive forces)] as another method for the determination of intermolecular force laws — to be used in conjunction with various other methods.[32]

From the practical, or engineering point of view, a proper determination of the interaction parameters contained in $I(\omega)$ will permit extrapolation to frequency regions which have not as yet been observed experimentally. One would thus have available a useful tool for the study of absorption in the so-called atmospheric "windows," in which absorption is usually dominated by the far-wings of strong bands.

B. There remains one further subject for future research, which has not been discussed as yet. Namely, as was noted in the introduction (Section 1), Burch et al[2] found that, in the high-frequency far wing of the self-broadened $3\nu_3$ band of CO_2, at 7000 cm^{-1}, the absorption coefficient $k(\omega)$, although sub-Lorentzian, is much higher than would be inferred from the comparable situation in the case of the fundamental ν_3 band in the vicinity of 2400 cm^{-1}. In what follows, certain speculations, which in our opinion are relevant for the explanation of this rather unique phenomenon, will be outlined. Briefly, we consider the two-stage process described by the questions,

$$CO_2^{(0)} + \hbar\omega \rightarrow CO_2^{(3)}$$

$$CO_2^{(3)} + CO_2^{(0)} \rightarrow CO_2^{(2)} + CO_2^{(1)} .$$

In these equations the superscript attached to CO_2 indicates the vibrational quantum number of the ν_3 branch (those of the other branches being zero throughout). The first stage occurs via electromagnetic interaction; the second may occur via dipole-dipole coupling (which is strongly allowed by harmonic-oscillator selection rules); also, the adjective "two-stage" (used above) implies that intermediate energy need not be conserved.

Now, in considering the physical significance of the above mechanism, we note the following important fact. Namely, the exponential-type fall-off characteristic of the present theory depends crucially upon the discrepancy between the energy of the absorbed light quantum and the vibrational energy of the absorbing system (as is clearly put in evidence by the occurrence of the quantity $(\omega-\omega_0)$ in the argument of the exponential factor in the formulae

of Section 2). With this fundamental point in mind, let us now note that, due to small anharmonicity, the vibrational energy of the final state $CO_2^{(2)} + CO_2^{(1)}$ turns out to be larger than that of intermediate state $CO_2^{(3)}$; in fact, from data in Herzberg's book, one finds that

$$\omega_{20} + \omega_{10} - \omega_{30} \approx 50 \text{ cm}^{-1}$$

so that in the high frequency far wing

$$\hbar\left[\omega - (\omega_{20} + \omega_{10})\right] < \hbar(\omega - \omega_{30}) ,$$

i.e., the two-stage reaction permits the realization of a smaller discrepancy between the energy of the absorbed quantum and that of the final vibrational state. From this result we are inclined to infer that the onset of the exponential fall-off would occur at higher values of $\omega-\omega_0$ than would be expected in the absence of this mechanism. As may be seen from Fig. 6, reference 2, this spectral behavior corresponds to the experimental observations.

The above remarks constitute the bare framework of an idea which we propose to use as a basis for the development of a theory which we hope will provide an explanation of the anomalous absorption observed by Burch for this case. In this connection, we have been encouraged by recent information from Burch (private conversation) that similar behavior has been observed for the high frequency, far wing of the self-broadened $3\nu_3$ line of N_2O. Examination of the relevant anharmonicity parameters in Herzberg's book indicates that here also the above described, two-stage process is energetically favored.

APPENDIX I

In this appendix the integral

$$\mathcal{J}_i = \frac{\alpha v_i}{4} \int_{-\infty}^{+\infty} \operatorname{sech}^2 \frac{\alpha v_i t}{2}\, e^{-i(\omega-\omega_0)t}\, dt \tag{I.1}$$

will be evaluated. To this end it is first convenient to introduce a new variable of integration

$$\xi = \alpha v_i t/2$$

and rewrite (I.1) as

$$\mathcal{J}_i = \frac{1}{2} \int_{-\infty}^{+\infty} \operatorname{sech}^2 \xi \; e^{-2i(\omega-\omega_0)\upsilon/\alpha v_i} \quad . \tag{I.2}$$

One then considers a clockwise integration over the rectangular contour whose corners are the points $-\infty$, $+\infty$, $+\infty - i\pi$, $-\infty - i\pi$. The integration over the top side ($-\infty \rightarrow +\infty$) gives (I.2). For the integration over the bottom side ($-i\pi \rightarrow -\infty + i\pi$), one notes that (a) the $\operatorname{sech}^2\psi$ factor remains unchanged, (b) the exponential factor gets multiplied by a constant $e^{-2\pi(\omega-\omega_0)/\alpha v_i}$ and the sign is negative; the result is then $-e^{-2\pi(\omega-\omega_0)/\alpha v_i}$. Since the contributions of the vertical sides are zero (by virtue of the $\operatorname{sech}^2\xi$ factor), one has

$$\mathcal{J}_i = \frac{1}{1 - e^{-2\pi(\omega-\omega_0)/\alpha v_i}} \; \mathcal{I}_i \; ; \tag{I.3}$$

$$\mathcal{I}_i = \frac{1}{2} \int_{C_p} \operatorname{sech}^2 \xi \; e^{-2\pi(\omega-\omega_0)\xi/\alpha v_i} \, d\xi \quad ,$$

where C_p denotes a counter-clockwise integration around a small circle the center of which is the single pole of the integrand (within the original rectangle) at the point $\xi = -\pi i/2$. Expanding $\mathrm{sech}^2\xi$ in the neighborhood of $\xi = -\pi i/2$, one has (with $\xi = -\frac{\pi i}{2} + z$)

$$\mathcal{J}_i = \frac{1}{2} e^{-\pi(\omega-\omega_o)/\alpha v_i} \int_{C_p} \frac{e^{-2i(\omega-\omega_o)z/\alpha v_i}}{z^2} dz$$

$$= \frac{2\pi(\omega-\omega_o)}{\alpha v_i} e^{-\pi(\omega-\omega_o)/\alpha v_i)} , \qquad (I.4)$$

which, together with (I.3), yields

$$\mathcal{J}_i = \frac{2\pi(\omega-\omega_o)}{\alpha v_i} \frac{e^{-\pi(\omega-\omega_o)/\alpha v_i}}{1-e^{-2\pi(\omega-\omega_o)/\alpha v_i}} . \qquad (I.5)$$

APPENDIX II

The subject matter of this appendix is the derivation of an expression for the probability distribution of the relative velocity of two colliding atoms, one of which is a constituent of a triatomic linear molecule. For the sake of definiteness we consider the text case of a noble-gas atom, e.g., argon, colliding with one of the oxygen atoms of CO_2. One task is then to derive (2.39), i.e.,[33]

$$P(v) = \frac{1}{(2\pi v_T^2)^{1/2}} e^{-v^2/2v_T^2} \qquad \text{(II.1)}$$

where v is the component of relative velocity of colliding noble gas and xoygen atom, together with an explicit expression for v_T^2; the calculation will also yield [cf.text subsequent to Eq. (2.43)] an expression for the reduced mass, M.

The starting point of the calculation is an expression for the probability distribution of the various elementary velocities involved in the problem, to wit

$$P(\underline{v}_A, \underline{v}_g, \underline{v}_r)\, d^3\underline{v}_A d^3\underline{v}_g d^2\underline{v}_r$$

$$= \left[\frac{d^3\underline{v}_A}{\left(2\pi v_{TA}^2\right)^{3/2}} e^{-v_A^2/2v_{TA}^2}\right]\left[\frac{d^3\underline{v}_g}{\left(2\pi v_{Tg}^2\right)^{3/2}} e^{-v^2/2v_{Tg}^2}\right]$$

$$\times\left[\frac{d^2\underline{v}_r}{2\pi v_{Tr}^2} e^{-v_r^2/2v_{Tr}^2}\right] . \qquad \text{(II.2)}$$

In this expression, $\underline{v}_A$, $\underline{v}_g$, and $\underline{v}_r$ respectively denote the vector velocities of the noble-gas atom, the center of gravity of the CO_2 molecule, and the rotational velocity of said molecule. The notations $d^3\underline{v}_A$ and $d^3\underline{v}_g$ refer to the three-dimensional (cartesian) volume-elements of $\underline{v}_A$ and $\underline{v}_g$; the notation $d^2\underline{v}_r$ takes account of the fact that, by virtue of the condition

$$\underline{v}_r \cdot \underline{n} = 0 \quad , \tag{II.3}$$

there are only two independent components of rotational velocity, both perpendicular to $\underline{n}$.

On the r.h.s. of (II.2), the constants v_{TA}, v_{Tg}, and v_{Tr} are given by the formulae

$$v_{TA}^2 = kT/M_A \tag{II.4a}$$

$$v_{Tg}^2 = kT/M_g = kT/M_{CO_2} \tag{II.4b}$$

$$v_{Tr}^2 = \frac{kTR_{CO}^2}{I} = \frac{kT}{2M_0} \tag{II.4c}$$

In the case of the first two square brackets, the insertion of (II 4a) and (II 4b) yield the manifestly correct Boltzmann distributions (the factors $\left(2\pi v_A^2\right)^{-3/2}$ and $\left(2\pi v_g^2\right)^{-3/2}$ taking care of the normalizations).

The third square bracket, describing the distribution of the rotational velocity, requires some comment. First of all, we note the obvious feature of its difference in form from the other two brackets; this difference arises solely from the above-noted two-dimensional character of the motion. In order

to clarify the bracket further, we note that it may be written in the form

$$P(\omega)d^2\underline{\omega} = \frac{d^2\omega}{2\pi\omega_{Tr}^2}\, e^{-R_{CO}^2\omega^2/2v_{Tr}^2}$$

($\underline{\omega}$ = angular velocity)

which, with the use (II.4c), becomes

$$P(\underline{\omega})d^2\underline{\omega} = \frac{d^2\underline{\omega}}{2\pi\omega_{Tr}^2}\, e^{-I\omega^2/2kT} \tag{II.5}$$

with

$$\begin{aligned} {}^{2}_{Tr} &= v_{Tr}^2/R_{CO}^2 \\ &= kT/I \ , \end{aligned} \tag{II.6}$$

and where the notation $d^2\underline{\omega}$ takes note of the fact that $\underline{\omega}$ is also a two-dimensional vector, perpendicular to the molecular axis, $\underline{n}$.

Equation (II.5) already begins to resemble the standard expression; in particular with respect to the Boltzmann factor, $e^{-I\omega^2/2k_T}$. In order to achieve an even more familiar form, let us go over to a two-dimensional polar coordinate system, in which $\underline{\omega}$ is expressed in terms of its magnitude, and angle, ϕ, with respect to an axis perpendicular to $\underline{n}$, but otherwise arbitrary; then, upon using the formula $d^2\underline{\omega} = \omega d\omega d\phi$ and integrating over Φ, one obtains the standard angular-velocity distribution function

$$P(\omega)d\omega = \frac{I\omega d\omega}{kT}\, e^{-I\omega^2/2kT} \ , \tag{II.7}$$

or, in terms of angular momentum, $J = I\omega$

$$P(J)dJ = \frac{JdJ}{IkT} e^{-J^2/2IkT} . \tag{II.8}$$

It should finally be remarked that the third bracket of the r.h.s. of (II.2) may be obtained from the fundamental prescription of statistical mechanics, which, for the case of rotational motion, reads

$$P(\theta,\phi;p_\theta,p_\phi)d\phi d\theta dp_\phi dp_\theta = \frac{1}{z} e^{-H_r/kT} d\phi d\theta dp_\phi dp_\theta , \tag{II.9}$$

where

$$H_r = \frac{1}{2I}\left[p_\theta^2 + p_\phi^2/\sin^2\theta\right]$$

is the rotational Hamiltonian, $d\phi d\theta dp_\phi dp_\theta$ is a differential volume element in the four-dimensional phase defined by the rotational coordinates θ, ϕ, and associated canonical momenta, p_θ and p_ϕ, and z is the partition function (which will not be written down explicitly here, since from our point of view it is merely a normalizing coefficient). Briefly, the procedure is transform from the canonical momenta to the associated velocities, via the formulae

$$v_\theta = R_{CO}\dot{\theta} = \frac{R_{CO}}{I} p_\theta \tag{II.11a}$$

$$v_\phi = R_{CO}(\sin\theta)\dot{\phi} = \frac{R_{CO}}{I\sin\theta} p_\phi , \tag{II.11b}$$

thereby obtaining[34]

$$P(\theta,\phi;p_\theta,p_\phi)d\theta d\phi dp_\theta dp_\phi = \frac{I^2}{zR_{CO}^2} e^{-(I/R_{CO}^2)\left[v_\theta^2+v_\phi^2\right]/2kT} . \tag{II.12}$$

Note, now that (II.12) is equal to the typical spatial volume element $d\Omega_n = \sin\theta d\theta d\phi$ (defining the direction of $\underline{n}$) multiplied by a factor which, in view of (II.4c), may be written as

$$P(v_\theta,v_\phi)dv_\theta dv_\phi = (\text{const})\, e^{-\left[v_\theta^2+v_\phi^2\right]/2v_{Tr}^2}\, dv_\theta dv_\phi \,. \qquad \text{(II.13)}$$

Since the direction of v_θ and v_ϕ are both perpendicular to $\underline{n}$ (as well as to each other), the r.h.s. of (II.13) is in fact equal (apart from a normalization constant) to the third bracket of (II.2), q.e.d.

With these preliminary remarks on the validity of (II.2) out of the way, we now proceed to a second basic formula, namely, the relationship between v and the vector velocities occurring in (II.2). Remembering that v denotes the component of relative velocity of colliding atoms (in our example the noble-gas perturber h one of the oxygen atoms of CO_2) parallel to the line-of-centers of said a oms (i.e., to $\underline{n}_c$), we have

$$v = (\underline{v}_A-\underline{v}_g-\underline{v}_r)\cdot\underline{n}_c \,,$$

which, upon going over to a cartesian system whose z-axis is parallel to the molecular axis, $\underline{n}$, may be written as

$$\begin{aligned} v = \; & n_{cx}(v_{Ax}-v_{gx}-v_{rx}) + n_{cy}(v_{Ay}-v_{gy}-v_{ry}) \\ & + n_{cz}(v_{Az}-v_{gz}) \,, \end{aligned} \qquad \text{(II.14)}$$

one notes the absence of the term linear in v_{rz} since, with $\underline{n}$ along the z-axis (II.3) becomes $v_{rz} = 0$.

In proceeding further, it is expedient to go over to a more general notation, in which (II.2) is written in the form

$$P(\ldots.v_i\ldots.)dv_1\ldots.dv_i\ldots = \prod_{i=1}^{8}\left[\frac{dv_i}{(2\pi v_{Ti}^2)^{\frac{1}{2}}}\; e^{-v_i^2/2v_{Ti}^2}\right] , \qquad (II.15)$$

where i refers to the cartesian components of the various velocities. For the sake of definiteness, i = 1,2,3 denote the x,y,z components of $\underline{v}_A$, i = 3,4,5 the corresponding components of $\underline{v}_g$, and i = 7,8 the x,y components of $\underline{v}_r$ Inspection of relations (II.4a,b,c) then show that

$$v_{T1}^2 = v_{T2}^2 = v_{T3}^2 = kT/M_A \qquad (II.16a)$$

$$v_{T4}^2 = v_{T5}^2 = v_{T6}^2 = kT/M_{CO_2} \qquad (II.16b)$$

$$v_{T7}^2 = v_{T8}^2 = kT/2M_r \qquad (II.16c)$$

In this new notation (II.14) may be written as

$$v = \sum_i a_i v_i \quad , \qquad (II.17)$$

where

$$a_1 = a_4 = a_7 = n_{cx} \qquad (II.18a)$$

$$a_2 = a_5 = a_8 = n_{cy} \qquad (II.18b)$$

$$a_3 = a_6 = n_{cz} \quad . \qquad (II.18c)$$

The normalized expression for $P(v)$ is now written as

$$P(v) = \int dv_1 \; .....\int dv_8 \;\; P(....v_i....)\delta(v-\sum_i a_i v_i) \quad . \tag{II.19}$$

Equation (II.19) expresses the fact that $P(v)$ is gotten by integration over all values of v_i which are subject to the constraint imposed by (II.17) (and incorporated in (II.19) by the delta-function). Expressing the delta-function in its Dirichlet representation

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ixt}\, dt$$

and utilizing (II.15), one then has

$$P(v) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\; e^{ivt} \; \pi_i \left[\int_{-\infty}^{+\infty} \frac{dv_i}{(2\pi v_{Ti}^2)^{\frac{1}{2}}} \; e^{-v_i^2/2v_{Ti}^2 \; - \; ita_i v_i}\right] . \tag{II.20}$$

The evaluation of the velocity integrals is standard; one obtains for each square bracket in (II.20) a factor $e^{-t^2 v_{Ti}^2 a_i^2}$ so that (II.20) becomes

$$P(v) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ivt}\; e^{-t^2 v_T^2/2}\; dt \quad , \tag{II.21}$$

where

$$v_T^2 \equiv \sum_i a_i^2/v_{Ti}^2 \quad . \tag{II.22}$$

The t-integration is now done, yielding,

$$P(v) = \frac{1}{(2\pi v_T^2)^{\frac{1}{2}}} e^{-v^2/2v_T^2} \tag{II.23}$$

which is identical to (II.1), q.e.d. Moreover, the required explicit expression for v_T^2 is given by (II.22), in conjunction with formulae (II.18a,b,c) and (II.16a,b,c). Combining these relationships one has, without further ado

$$v_T^2 = kT\left[\frac{1}{M_A} + \frac{1}{M_{CO_2}} + \frac{1}{2M_0}\sin^2\theta\right] \quad , \tag{II.24}$$

where, with θ the angle between $\underline{n}_c$ and the z axis — that is, between $\underline{n}_c$ and the molecular axis $\underline{n}$, the obvious relation

$$\sin^2\theta = n_{cx}^2 + n_{cy}^2 = (\underline{n} \times \underline{n}_c)^2$$

has been used.

We may now note briefly that (II.24) used in conuunction with the text relationship

$$v_T^2 = kT/M$$

yields for the reduced mass, M, the expression

$$\frac{1}{M} = \frac{1}{M_A} + \frac{1}{M_{CO_2}} + \frac{1}{2M_0}\sin^2\theta \quad . \tag{II.25}$$

REFERENCES

1. B.H. Winters, S. Silverman, and W.S. Benedict, J. Quant. Spectroscopic Radiation Transfer, Vol. 4, 527 (1964).

2. D.E. Burch, D.A. Gryvnak, R.R. Patty, and C.E. Bartky, J. Opt. Soc. Am. 59, 267-280 (1969).

3. It should be mentioned that a treatment of far-wing absorption due to rotational perturbations was given in our previous ONR report (S. Altshuler, D. Arnush, L.M. Frantz, T.D. Holstein, "High Intensity Laser Propagation in the Atmosphere," TRW Semiannual Report 05691-6005-R000, 1 March 1967 - 31 August 1967, especially Chapter I), for the case of a pure rotational band. However, in the present work, the spectral frequency, ω, obeys the condition $\omega_{rot} << |\omega-\omega_0| << \omega_0$ (ω_0 = vibrational frequency), in contrast to the case treated in the cited report, wherein $\omega_0 = 0$; this difference turns out to effect a profound modification of the magnitude and frequency-dependence of the absorption.

4. S. Altshuler, D. Arnush, L.M. Frantz, T.D. Holstein, "High Intensity Laser Propagation in the Atmosphere," TRW Final Report 05691-6003-R000, 1 Nov 1965 - 28 Feb 1967, especially Chapter I.

5. T.D. Holstein, Phys. Rev. 79, 774 (1950).

6. Specifically, it is the matrix element of the dipole moment operator between the initial and final vibrational states; here, and in what follows, the manifestly valid approximation of taking μ_0 constant will be employed.

7. This assumption is appropriate when the J-values associated with the transition are high (as in the case of CO_2). It should be remarked, however, that the approximation also implicitly assumes the rotational Hamiltonians of the initial and final vibrational states to be the same, i.e., equal moments of inertia. In the case of the CO_2 lines investigated in the cited experiments[1,2] there exist slight departures from said equality (as is evidenced by the existence of band-heads for these lines). It is, however, anticipated (and hopefully to be shown in the future) that the applicability of the present calculation to CO_2 will not be invalidated by these departures (which are relatively very small indeed).

8. As will be seen, if the number of optically-effective collisions in the interval $-T/2 \leq t \leq T/2$ is large (as is the case, since T is arbitrarily large), the contribution of the integrated terms at $\pm T/2$ is relatively negligible. Actually they constitute a spurious artifact of the theory, in that the basic equation (2.2) implies the sudden "switching-on-and-off" of the electromagnetic field at times $t = \pm T/2$. As is known, terms arising from such formulations have no physical significance.

9. For the time being, it is assumed that these are dominant. The inclusion of long-range interactions is reserved for a future investigation.

10. In writing down (2.14), the higher-order terms associated with $\underline{A}^{(3)}(\omega)$, etc., have been neglected.

11. It may be pointed out, in passing, that $(\ldots\ldots)_i$ is [cf. (2.8), (2.10) and the second sentence after Eq. (2.15)] 90° out of phase with the retained term; hence its contribution to $I(\omega)$ is quadratic in the smallness parameter $|\omega_p/(\omega-\omega_0)|$

12. Cf. P.W. Anderson, Phys. Rev. 76, 647-661 (1949); also, C.J. Tsao and B. Curnutte, J. Quant. Spectrosc. Radiat. Transfer 2, 41-91 (1962), which constitutes an augmented exposition of Anderson's work.

13. P.W. Anderson, reference 12, especially the last paragraph of page 649, to the effect that the individual (rotational) components of a composite line must be well separated. (The alternate possibility states by him that the width exceed the separation of the components is irrelevant for the situation encountered in the cited experiments[1,2].) In our opinion, the additional stipulation given by the text Eq. (2.21) is required. For this, Anderson's condition is necessary but not sufficient.

14. Strictly speaking, our $\underline{\Delta\omega_i}$ represents the impact-induced alteration of rotational frequency. Generally, however, this may be expected to be of the order of thermally-accessible rotational frequencies, i.e., essentially the rotational spread of the band. Anderson's theory, on the other hand, applies to a particular rotational component of a vibrational band. [In this connection, we have perpetrated somewhat of a swindle in writing down (2.19), in that ω_0 should be replaced by a symbol denoting a particular rotational component. However, as noted above in Section 1, the usual practice of experimentalists in analyzing their data, namely by comparing them with a "theoretical" $I(\omega)$, taken as a sum of Lorentzian contribution from the individual lines, leads to (2.19) in the far-wing region (as defined by (2.22).]

15. Specifically, this will involve the replacement of $\delta(t-t_1)$ in (2.6) by a suitable finite-width function.

16. The time-dependence of this relative velocity will shortly be shown to be intimately linked up with (in fact essentially identical to) that of $\underline{\omega}_p$ in a collision interval.

17. The r.h.s. of (2.25) is obtained from the more basic relation

$$v = (2/M)^{\frac{1}{2}} \left(E - V\, e^{-\alpha x}\right)^{\frac{1}{2}}$$

(where M is the appropriate reduced mass) by factoring from the square root the initial "normal" energy, $E \equiv \frac{1}{2} M v_0^2$, and introducing $x_c = \frac{1}{2} \log \frac{V}{E}$.

18. In the case of a noble gas of intermediate mass, such as argon, one may take $v_{rot}/v \sim 1/\sqrt{2}$; the smallness parameter is then $\sim 1/5\cdot 6$.

19. Incidentally, preliminary considerations indicate that said corrections are quadratic in $\left(\frac{v_{rot}}{v} \frac{1}{2R_{CO}}\right)$.

20. Within the framework of (2.24) and (2.27), the overall frequency change, $\Delta\underline{\omega}_i$, is simply equal to $(R_{CO}/I)\underline{n}_i \times \int \underline{F} dt$; explicit values may always be obtained by going to the impact limit ($\alpha \to \infty$) and using standard methods of classical mechanics (as is, in fact, done in the latter part of this section)

21. It will be noted that the factor $\left(\frac{\alpha v_i}{4}\right) \operatorname{sech}^2\left[\alpha v_i (t-t_i)/2\right]$ reduces to $\delta(t-t_i)$ in the limit $\alpha \to \infty$, i.e., in the limit in which the repulsive potential becomes that between two hard spheres. For such a potential collisions are clearly pure impacts. In the case of finite α, it is also clear that $\tau_c \gtrsim 2/\alpha v_i$

22. This statement is based on preliminary studies which also indicate that the contribution of $(\ldots\ldots)_i$ is quadratic in the new parameter A systematic study is reserved for the future.

23. Since v_i appears in the rapidly varying exponential factor of (2.38), we believe that the thermal average is the most important. In particular, as will be seen below, it leads to an exponential factor whose argument is fractional in $(\omega-\omega_0)$, rather than linear [as is superficially exhibited by (2.38)].

24. More generally, it is being asserted that the distribution of the projection of an arbitrary sum of velocities along an arbitrary direction obeys (2.39), with a suitably chosen v_T^2. This assertion is easily proved for the case when all the component velocities refer to purely linear motion. Its proof for the case when one of the components is rotational is somewhat more subtle, and will be given in Appendix II. It is also subject to the limitation of (2.27); only within that limitation is it possible to regard the rotational motion as linear.

25. It is here presumed that the rotational velocity is also involved in the thermal average.

26. All other masses have appropriate subscripts attached to them, so no notational problems arise.

27. Under the assumption [incorporated by Eq. (2.23)] that the interaction between the perturber and the molecule is a sum of spherical interaction between the perturber and the individual atomic constituents, and with the condition expressed by (2.24), it is clear that only perturber-oxygen collisions contribute to nonvanishing $\Delta\underline{\omega}_i$'s.

28. A similar effect is known to exist for the very analogous case of vibrational deactivation (cf. K. F. Herzfeld and T.A. Litovitz, Absorption and Dispersion of Ultrasonic Waves, Acad. Press Inc., New York, 1959, pp. 278-285.

29. If one expresses $1/\tau$ in wave numbers (which is equivalent to replacing it by γ) and expresses frequencies also in wave numbers, $k(\omega)$ comes out in units of cm^{-1} atm^{-2} (STP), as is to be expected since it is proportional to the product of densities of absorbing and perturbing gases.

30. Alternatively, we can recalculate the theoretical $k(\omega)$ by taking $\omega-\omega_0$ = 210 cm^{-1} (corresponding to ω = 2560 cm^{-1}, at which an actual measurement was made); it turns out that $\langle\,.\,\rangle_{coll}$ gets increased by a factor of (2.86), which together with a factor $(250/210)^2$ (which accounts for the change in $(\omega-\omega_0)^{-2}$), yields a theoretical $k(\omega)$ of 2.7 x 10^{-7} cm^{-1} atm^{-2}, to be compared with Burch's value, ~ 2.4 x 10^{-6} cm^{-1} atm^{-2}. Thus the theoretical $k(\omega)$ is still lower than the experimental value by a substantial factor ($\stackrel{\sim}{=}$ 10).

31. It may also be remarked that the average theoretical slope of $\log_e\left[\langle\cdots\rangle_{coll}\right]$ vs $(\omega-\omega_0)$, in the range between 210 cm^{-1} and 250 cm^{-1} is $\approx$ .026 cm, whereas the corresponding experimental slope (as closely as we are able to estimate it from Fig. 14 of Ref. 2) is $\approx$ .014 cm. However, in this region, experimental uncertainties are substantial; moreover, (and more importantly) the theory in its present form requires much further development (and refinement) for a comparison of such details as slopes to be of any real significance.

32. For a review of these, see Advances in Chemical Physics, Vol. 12: Intermolecular Forces, edited by J.O. Hirschfelder (Interscience Publishers, 1967).

33. The subscript, i, in (2.39), is dropped for convenience.

34. Note that in relating the differentials of the momenta to those of the associated velocities, the coordinates ϕ and θ are held constant

CHAPTER II

BEAM DYNAMICS

I. INTRODUCTION

This report is concerned with the effect of target motion on thermal self-defocusing. In a previous study[1] we have produced a description of the self-defocusing effect applicable only to the case of a stationary target, that is, to the situation in which the laser beam heats a fixed air mass throughout the entire pulse period. If the target is moving, however, the beam must be rotated, and a given air mass is heated only for the time required for the beam to pass through it; consequently, there must be less defocusing.

It was found that for a stationary target the limitation caused by self-defocusing is on the total amount of energy that can be delivered to the target. However, for a moving target we expect the limitation to be on the deliverable power. The reason there is no limitation on the total energy is simply that new air masses are constantly being used for the beam path, so there is no cumulative heating. By analogy to the stationary-target case we expect a limitation on the energy deliverable through any given air mass, so the maximum transmittable power depends on how rapidly the beam rotates. The amount of time a particular air mass is heated depends on its distance from the laser, and is smallest at the target distance (its value there is simply the beam width divided by the target velocity). Therefore, we can obtain a simple overestimate of the maximum transmittable power from the energy limit calculated in the stationary target case[1], namely, the latter energy divided by the heating time at the target.

In this report we obtain a more precise estimate of the maximum transmittable power by extending the stationary-target analysis. The extension is

somewhat crude, but it at least accounts for the dependence of the heating time of any air mass on its distance from the laser. The crudity lies in the way that we treat the beam rotation. Instead of solving equations that properly describe a beam continuously rotating into new regions of air, we use the equations that describe a stationary beam; we simulate the rotation by assigning to the air at any given distance from the laser a heating interval estimated from the time it would take a rotating beam to pass through it.

The stationary-beam analysis is based on the ray optics approximation, that is, diffraction spreading is ignored. In addition, it is assumed that the time required for the beam to pass through any air mass is longer than the time required for sound to propagate in air across the beam. Furthermore, another approximation is made, which significantly simplifies the mathematical system. An integral which appears in the equations, namely the time integral of the light flux at any point in space, is replaced by the simple product of the instantaneous flux and the time. As a result the time becomes a trivial parameter instead of an independent variable, and the equations become soluble for a certain special case. Now, in the extension described in this report, what we have done to simulate the beam rotation is to replace the actual time (in this product of flux and time) by the time interval over which the air mass at the point in question has been illuminated. Although this time interval now depends on one of the independent variables, namely, the distance from the laser, we find that the equations are still soluble for the same special case as before.

The particular manner in which the beam spreads by self-defocusing has been found to depend on the specific shape of its initial power profile. For example, if the power profile is uniform in the center and falls off only at the edges, then initially the rays in the uniform interior will not deflect at all, but the rays at the edge will peel off and deflect outwards. Thus the way that the beam degenerates is that the beam edge gradually erodes.

In this and the previous report[1] we have studied the rate at which the beam edge eats its way in to the interior. To do so we have considered the special case of an initial flux distribution having the shape indicated in Fig. 1. Because we are basically interested only in the behavior of the edge of the beam, we have chosen a planar geometry (for which the equations have a somewhat simpler form) rather than the more realistic cylindrically symmetrical geometry. The initial power profile is taken to be uniform along the negative axis, and to fall off exponentially along the positive axis.

We have obtained a solution to the equations which shows that the interior rays (the rays originating along the negative axis) go undeflected for a certain distance, then begin to deflect outwards (towards the positive axis). This behavior is indicated in Fig. 2 The solution is valid only in certain regions of space, but for any ray it is correct up to and including the point at which the ray starts to deflect. Therefore, it provides a first order description of the desired rate at which the beam edge erodes. We cannot obtain from our solution the trajectories of the rays after they begin to peel off.

The distance from the laser at which any ray begins to deflect depends, among other things, upon its original distance in from the edge, upon the beam

intensity, and upon the assumed distance-dependence of the period for which any air mass is illuminated. The illumination period in turn depends upon the angular velocity at which the laser beam is rotated.

For the model we have used, the degradation of the beam is due solely to the erosion of the outer edge. The interior region is entirely undegraded; that is, the flux in the interior is undiminished. Without the introduction of additional conditions into the problem the choice of a criterion for when the beam has lost its destructive capabilities is left somewhat arbitrary. For the sake of providing a definite example we have required that the edge may be permitted to eat its way in by no more than half the original beam radius. Using this condition we obtain a simple expression for the maximum flux which the self-defocusing effect allows us to transmit through the atmosphere. The expression depends upon such parameters as the beam intensity, the beam diameter, the target distance, the rotational rate of the beam, and the effective absorption coefficient for heating of air by light at the laser frequency.

In summary it should be emphasized that our solution contains a number of approximations and limitations, which have been mentioned above. Removing the approximations and limitations would probably require an extensive computer analysis. The major value of our result relative to such an analysis is that, being analytical, it provides a single expression from which one can easily estimate the maximum transmittable power under a variety of circumstances. We shall give some illustrative examples in a later section.

2. DERIVATION OF THE EQUATIONS

In this section we derive the equations which describe the propagation of the light rays in a medium whose optical properties are themselves determined by heating due to the presence of the light. Most of this derivation constitutes only a minor modification of the work in reference (1). The principal difference, as discussed in the previous section, lies in the introduction of a position-dependent illumination period for the purpose of simulating the beam rotation.

We assume a planar geometry with the z-axis normal to the laser face, the x-axis parallel to the laser face, and all quantities being independent of the third coordinate. The laser face is in the $z = 0$ plane, so that z is the coordinate denoting distance from the laser along the propagation direction, and x is the transverse coordinate. The ray trajectories in a medium of refractive index n are described by the eikonal equation. One of the standard forms in which the latter may be written is

$$\left(\frac{\partial n\hat{a}}{\partial \sigma}\right)_s = \nabla n \quad , \tag{2.1}$$

where $\hat{a}$ is a unit vector tangent to the ray path at any point, σ is the path length along a given ray, and s is the value of the transverse coordinate of any ray at $z = 0$, that is, $x(s, z = 0) = s$.

It will be convenient to use, instead of the (x,z) coordinate system, one defined by the planes of constant z and the surfaces generated by the ray paths (surfaces of constant s), which are the solutions to the problem. Also, we shall confine ourselves to situations in which the rays deviate from their

initial directions only by small angles. Therefore, by taking the projection of the vector equation (2.1) along the transverse axis, transforming to the (s,z) coordinate system, and making the small-angle approximation, we obtain the ray equation

$$\frac{\partial x}{\partial s}\ \frac{\partial^2 x}{\partial z^2} = -\frac{\partial}{\partial s}\left(\frac{n_a - n}{n_a}\right) \quad , \tag{2.2}$$

where $n_a(s,z)$ is the ambient value of the refractive index.

The conservation of energy flux F is stated by (assuming negligible absorption losses in the atmosphere, and using the small-angle approximation)

$$F(s,z,t)dx = F(s,0,t)ds \quad . \tag{2.3}$$

This follows from the fact that the surfaces of constant s are everywhere tangent to the ray paths, so that no flux escapes through them. The line element dx is the separation at height z between two rays which are initially separated by ds, so we may use the relation $dx = (\partial x/\partial s)ds$ to obtain from (2.3) the flux conservation equation,

$$F(s,z,t) = \frac{F(s,0,t)}{\partial x/\partial s} \quad . \tag{2.4}$$

Our neglect of absorption losses is quite justifiable for ruby and neodymium lasers, for which the energy loss in passing vertically through the entire atmosphere is no more than about one percent. For a CO_2 laser about 0.3 of the incident energy is absorbed in the atmosphere. This loss is not insignificant, but for our purposes it is not great enough to warrant the additional complications of accounting for it in the conservation equation.

Next we need the relation between the flux and the refractive index. The rate of change of refractive index is proportional to the rate of change of the density, which is proportional to the rate at which heat is deposited in the atmosphere; the latter in turn is proportional to the flux. The refractive index for a dilute gas is given by

$$n-1 = 2\pi\rho\alpha \quad , \tag{2.5}$$

where ρ is the molecular number density and α is the molecular polarizability. Consequently, we have

$$\frac{dn}{dt} = 2\pi\alpha \frac{d\rho}{dt} = \frac{n-1}{\rho} \frac{d\rho}{dt} \quad . \tag{2.6}$$

The density changes according to the equation of state of an ideal gas,

$$PV = NKT \quad , \tag{2.7}$$

where $\rho = N/V$, and where K denotes Boltzmann's constant. We shall assume that the heating takes place at constant pressure, so that from (2.7) we obtain

$$\frac{1}{\rho} \frac{d\rho}{dt} = - \frac{1}{V} \frac{dV}{dt} = - \frac{NK}{PV} \frac{dT}{dt} \quad . \tag{2.8}$$

The assumption of isobaric heating is valid only if the times of interest are large compared with the time required for sound to traverse the heated region.[1] The velocity of sound in air is about 3×10^4 cm/sec, so it

would take several milliseconds to cross a beam a meter in diameter. This means that if we are considering a stationary target the pulse length must be greater than several milliseconds, or less for a smaller beam. For a moving target we have the additional constraint that the beam must rotate sufficiently slowly that it is effectively stationary during a sound traversal time. It may easily be seen that this constraint is equivalent to the requirement that the target velocity be somewhat less than the velocity of sound in air. Therefore our results will be applicable only to the illumination of subsonic targets. The direction in which our results err for supersonic targets is easy to see. When a region of atmosphere is heated, a finite amount of time is required for the density change to develop. This is the time needed for sound to cross the heated region. Over a shorter period the density change and therefore the refractive index change, is much less than what we estimate under the assumption of heating at constant pressure. Consequently the defocusing effect will be smaller than estimated. As a result, the amount of flux that can be transmitted in the case of a supersonic target will be greater than the upper limit which we shall predict.

To continue, the temperature increase dT for an amount of heat dQ deposited at constant pressure in a volume V of air is

$$dQ = C_p dT \quad , \tag{2.9}$$

where C_p is the specific heat at constant pressure. Now if we denote by k the effective absorption coefficient for heating of air by the laser light, then the amount of heat per unit volume per unit time deposited due to beam absorption is given by kF. Therefore, from (2.9) we obtain

$$kF = \frac{1}{V}\frac{dq}{dt} = \frac{C_p}{V}\frac{dT}{dt} \quad . \tag{2.10}$$

Now, combining (2.10), (2.8) and (2.6), and using the well known ideal gas relation,

$$NK = C_p - C_V \quad , \tag{2.11}$$

C_V being the specific heat at constant volume, we obtain the desired relation between refractive index and flux,

$$\frac{dn}{dt} = -\frac{(n-1)(\gamma-1)kF}{\gamma P} \quad , \tag{2.12}$$

where $\gamma = C_p/C_V$. For air the ratio of specific heats is $\gamma = 1.4$. Eq.(2.12) may be integrated to give

$$n(s,z,t) - n_a = -\frac{(\gamma-1)(n_a-1)k}{\gamma P}\int_{x,z} F\left[(s(x,z,t),z,t\right]dt \quad , \tag{2.13}$$

where n_a is the ambient value of the refractive index in the absence of the beam. The factor n-1 on the right hand side of (2.12) has been assigned the fixed value n_a-1 and removed from the integral, since, as may be easily verified, the fractional change in n is negligible compared to unity. The subscript x,z on the integral sign emphasizes that the relation (2.12) applies to a fixed air mass, and therefore to a fixed point in space (x,z). Since, because of continued heating of the air, the ray trajectories change with time, the origin coordinate s(x,z,t) of the ray passing through the point (x,z) also changes with time. Thus, in the integral F depends on t not only explicitly, but also implicitly through the implied variation of s with time.

Now we make our most serious approximation. We assume that in the integral, F may be regarded as constant with respect to both t and s during the period for which the beam passes through the given air mass. We replace the integral by

$$\int_{x,z} F\left[s(x,z,t),z,t\right]dt \longrightarrow F(s,z,t)\tau(z,t) \quad , \tag{2.14}$$

where $\tau(z,t)$ is the time interval over which an air mass at distance z from the laser has been illuminated at time t. How well we simulate the rotation of the laser beam now depends on how judiciously we choose $\tau(z,t)$. In the special case of a stationary target we have $\tau(z,t) = t$.

Strictly speaking, the beam rotation should be described by time dependent boundary conditions on the rays. What we shall do here, as in the stationary-target case, is to let the $z = 0$ plane represent the laser face and require that the rays emerge normally from the laser face. That is, the angle made by the rays relative to the normal, $\theta = \partial x/\partial z$, must be zero at $z = 0$. To represent a rotating beam properly we must do something much more complicated mathematically. That is, we must require that the rays emerge normally from a plane which is rotating relative to a coordinate system fixed in the atmosphere. Our use of the approximation (2.14) eliminates this complication.

Now, according to (2.5) n_a-1 is proportional to ρ, the atmospheric density, and ρ decreases exponentially with altitude. However, according to the ideal gas law (2.7) the pressure P is also proportional to ρ. Consequently, in (2.13) the ratio $(n_a-1)/P$ is independent of density, and therefore of

altitude, so that the sea level values of n_a and P may be used. In general the altitude dependence of k, the effective absorption coefficient for heating, is considerably more complicated and uncertain. For example, for ruby lasers essentially all of the absorption is by water vapor, and for CO_2 lasers about half is by water vapor. The distribution of atmospheric water vapor, however, varies drastically from one geographical location to another, as well as from one time to another. Therefore, for the moment we shall simply regard k as an unspecified function of altitude, that is,

$$k = k(z\cos\phi) \quad , \tag{2.15}$$

where ϕ is the zenith angle at which the beam is propagating through the atmosphere at any instant of time.

We now have for the relation between the refractive index and the flux,

$$n(s,z,t) - n_a(z) = - \frac{(\gamma-1)(n_a-1)k(z\cos\phi)F(s,z,t)\tau(z,t)}{\gamma P} \quad . \tag{2.16}$$

Now, the system of equations which we wish to solve is composed of the ray equation (2.2), the flux conservation equation (2.4), and the relation between flux and refractive index (2.16). First we eliminate the flux between (2.4) and (2.16), and obtain a relationship between the value of the refractive index at any point (s,z) and its value along the same ray path but at the laser face,

$$n(s,z,t) - n_a(z) = \frac{n(s,0)-n_a(0)}{\partial x/\partial s} T(z,t) \quad , \tag{2.17}$$

where we have defined

$$T(z,t) = \frac{k(z\cos\phi)}{k_o} \frac{\tau(z,t)}{\tau(0,t)} , \tag{2.18}$$

and $k_o = k(0)$.

Next, it is convenient to define the dimensionless, positive quantity,

$$f(s,t) = \frac{n_a(0)-n(s,0,t)}{n_a(0)} , \tag{2.19}$$

so that (2.17) may be rewritten in the form [recall that n is so close to unity that unless index differences are involved we may write $n_a(z) = n_a(0)$]

$$\frac{n_a(z)-n(s,z,t)}{n_a(z)} = \frac{f(s,t)T(z,t)}{\partial x/\partial s} . \tag{2.20}$$

Now, physically, f(s,t) may be regarded as a reduced flux. To see this we use (2.16) and the definition (2.19) of f(s,t) and obtain

$$f(s,t) = \frac{(\gamma-1)(n_a-1)k_o\tau(0,t)}{\gamma P} F(s,0,t) . \tag{2.21}$$

Thus, f(s,t) is seen to have the same s-dependence as F(s,0,t). That is, it is proportional to the power profile at the laser face.

Finally, we may eliminate the refractive index by inserting (2.20) into the ray equation (2.2) to obtain

$$\frac{\partial x}{\partial s} \frac{\partial^2 x}{\partial z^2} \frac{1}{T(z)} = - \frac{\partial}{\partial s}\left[\frac{f(s)}{\partial x/\partial s}\right] \tag{2.22}$$

We have simplified the notation by suppressing the parametric t-dependence. To obtain the ray trajectories we must now solve (2.22) with the appropriate boundary conditions,

$$x(s,0) = s \quad , \tag{2.23a}$$

$$\theta(s,0) = \frac{\partial x}{\partial z}(s,0) = 0. \tag{2.23b}$$

3. SOLUTI[illegible]

Performing the derivatives in (2.22) and setting

$$x = s + x_1 \quad , \tag{3.1}$$

(so that x_1 is the transverse displacement of the ray originating at $x = s$) we may rewrite (2.22) in the form

$$\left(1 + \frac{\partial x_1}{\partial s}\right)^3 \frac{\partial^2 x_1}{\partial z^2} \frac{1}{T(z)} - f(s) \frac{\partial^2 x_1}{\partial s^2} + \frac{df}{ds}\left(1 + \frac{\partial x_1}{\partial s}\right) = 0 \ . \tag{3.2}$$

To solve (3.2) we shall make use of the following transformations of variables,

$$\frac{dp}{ds} = \frac{1}{\sqrt{f(s)}} \quad , \tag{3.3}$$

$$\frac{d\xi}{dz} = \sqrt{T(z)} \quad . \tag{3.4}$$

Actually, it will be useful to transform only selected terms in (3.2), so as to recast it in the form

$$\left(1 + \frac{\partial x_1}{\partial s}\right)^3 \left(\frac{\partial^2 X_1}{\partial \xi^2} + \frac{1}{2T^2} \frac{\partial T}{\partial z} \frac{\partial X_1}{\partial z}\right) - \frac{\partial^2 X_1}{\partial p^2} + \left(1 + \frac{3}{2} \frac{\partial x_1}{\partial s}\right) \frac{df}{ds} = 0 \quad , \tag{3.5}$$

where

$$X_1(p,\xi) = x_1(s,z) \quad . \tag{3.6}$$

We now assume that in (3.5) the $\frac{\partial x_1}{\partial s}$ terms and the $\frac{1}{2T^2} \frac{\partial T}{\partial z} \frac{\partial X_1}{\partial z}$ term may be dropped. Both of these terms vanish at the boundary plane $z = 0$,

because of the boundary conditions $x_1(s,0) = 0$ and $\theta(s,0) = \frac{\partial x_1}{\partial z}(s,0) = 0$. We shall see that in fact there exists a useful solution for which they vanish over an entire region of space; in that region of space the solution will be exact.

The approximate equation which we obtain from (3.5) is now

$$\frac{\partial^2 x_1}{\partial \xi^2} - \frac{\partial^2 x_1}{\partial p^2} + \frac{df}{ds} = 0 \quad . \tag{3.7}$$

Equation (3.7) is linear with constant coefficients, and can be solved in closed form. We shall not go through the details of solving it here; however, for completeness the procedure has been included in an appendix. The solution, with the required boundary conditions, is

$$x_1(s,z) = 2s - g(s,\xi) - g(s,-\xi) \quad , \tag{3.8}$$

where $g(s,\xi)$ is given by

$$\xi = \int_s^{g(s,\xi)} \frac{ds'}{\sqrt{f(s')}} \quad , \tag{3.9}$$

and ξ in turn is a function of z according to

$$\xi(z) = \int_0^z \sqrt{f(z')}\, dz' \quad . \tag{3.10}$$

The last equation follows from the transformation (3.4)

Now, the terms we have dropped do not vanish in general. It is only for a special choice of the initial power profile f(s) that they vanish in a region of interest. That special case was mentioned in the introduction and is illustrated in Fig. 1. The initial flux distribution is uniform along the negative axis, $s \leqslant 0$, which represents the interior of the more properly cylindrical beam. It falls off exponentially along the positive asix; the fall-off region represents the beam edge. Specifically, we have

$$f(s) = \begin{cases} a^2 , & s \leqslant 0 \\ a^2 \, e^{-2s/\lambda} , & s \geqslant 0 \end{cases} , \tag{3.11}$$

for times greater than $t = 0$. For $t < 0$, we assume the flux to be zero; that is, the beam is turned on at $t = 0$. The constant a^2, according to (2.21), is given by

$$a^2 = \frac{(\gamma-1)(n_a-1)k_o F_o \tau(0,t)}{\gamma P} , \tag{3.12}$$

where F_o is the (uniform) initial flux magnitude along the negative transverse axis.

It is easy to see physically why we expect that for this flux distribution the terms we have dropped from (3.5) will vanish over a finite region of space. Along the negative axis the flux is initially uniform, so the air will be heated uniformly. Consequently, the refractive index will change, but its change will be uniform with respect to the transverse direction, so there will be no transverse gradient. As a result, the light rays will initially not be bent, so the displacement x_1 will be zero; furthermore, the

uniformity will propagate in the z-direction. In the region where x_1 has the constant value zero, we have $\partial x_1/\partial s = \partial x_1/\partial z = 0$, so that the terms we have ignored actually vanish identically.

The situation is different along the positive transverse axis. The flux, and therefore the heating rate, is greatest at the beam edge ($s = 0$) and falls off for larger positive s. Therefore, the refractive index increases in the positive transverse direction. According to the eikonal equation (2.1), the rays deflect in the direction of increasing index. Therefore, they immediately begin to peel off in the positive transverse direction, which is equivalent to peeling off outward from a cylindrically symmetrical beam. As these outer rays peel off, the beam edge is displaced inwards (in the negative transverse direction) with increasing z, and the rays at the new edge peel off. Thus the rays in the region of initially uniform flux distribution propagate undeflected only for a limited distance, then they deflect outwards (in the positive transverse direction).

To see just how far they propagate undeflected we insert the explicit expression (3.11) for the initial flux distribution into the general solution (3.8, 3.9, 3.10) and obtain the explicit solution,

$$x_1(s,z) = \begin{cases} 0 \ , & s \leq -a\xi \\ s+a\xi-\lambda\log_e(1+s/\lambda+a\xi/\lambda) \ , & -a\xi < s \leq 0 \\ 2s+\lambda+a\xi-\lambda e^{s/\lambda}-\lambda\log_e\left|a\xi/\lambda+e^{s/\lambda}\right| \ , & 0 < s \leq \lambda\log_e(1+a\xi/\lambda) \\ 2s-\lambda\log_e\left|e^{2s/\lambda}-a^2\xi^2/\lambda^2\right| \ , & \lambda\log_e(1+a\xi/\lambda) < s \ . \end{cases} \tag{3.13}$$

Here $\xi(z)$ is understood to be a known function of z, determined from Eq. (3.10). To obtain an explicit expression for $\xi(z)$ we must first specify $T(z,t)$; doing so is equivalent to specifying the mean illumination time of an air mass at a distance z at time t. In order to get a feel for the properties of the solution (3.13) it is probably best to think of it in terms of the simple special case of a stationary target, with both the target and the laser at zero altitude. In this case we find from (2.18) that $T(z,t) = 1$, and as a result we have $\xi(z) = z$.

In the region $s \leq -a\xi(z)$, then, we have $\partial x_1/\partial z = \partial x_1/\partial s = 0$, so that in this region, as well as everywhere along the boundary plane $z = 0$, (3.13) is an exact solution of (3.5). Elsewhere, as we have said, the rays deflect, so that the terms we have dropped in going from (3.5) to (3.7) do not vanish. In fact, these terms quickly become sufficiently large that the solution (3.8) is not a good approximation except in and very close to the region $s \leq -a\xi(z)$. For $s \geq -a\xi(z)$, but $a\xi(z) - |s| \ll 1$, it may be seen that the neglected terms are still quite small, so that the solution is still quite accurate. From (3.13) we see that under these conditions the ray trajectories are

$$x_1(s,z) \simeq \frac{1}{2\lambda}(a\xi+s)^2 = \frac{1}{2\lambda}(a\xi-|s|)^2 . \tag{3.14}$$

Therefore, we find that the outer edge of the beam (the region of diverging rays) eats into the interior region (the region of initially uniform flux distribution) along the curve $s = -a\xi(z)$. That is, for any negative s, the corresponding ray propagates undeflected until it reaches a distance z from the laser face given by $\xi(z) = -s/a$; then it begins to diverge parabolically in $\xi(z)$ according to (3.14). This behavior is illustrated in Fig. 2.

It should be noted that the distance z at which an interior ray first begins to deflect does not depend on the steepness of the beam's original edge shape. However, once the ray begins to deflect, it does so more rapidly for a more steeply descending beam edge; more precisely, we see from (3.14) that the ray displacement x_1 is proportional to $1/\lambda$, where λ is the scale length for the exponential fall-off of the beam edge.

The region in which (3.14) is valid is quite small; from (3.14) we only learn the initial behavior of the rays when they begin to deflect. Since we do not know the details of how much the beam spreads once it does so, we must make a somewhat arbitrary choice of a criterion for when the beam is to be considered too degraded to be effective. Now, we have seen from the solution (3.13) that the beam interior is entirely undegraded, in the sense that the power density is undiminished; however, the beam edge moves steadily inward, so that the undegraded interior decreases in size. We assume that when the region of undiminished power density gets too small the beam is no longer useful. Therefore, if we denote by s_0 the maximum distance which we can tolerate having the beam's edge eat into its interior, then from

$$\xi(z) = s_0/a \tag{3.15}$$

and the definition (3.12) of a, we find

$$F_0 = \frac{\gamma P s_0^2}{(\gamma-1)(n_a-1)k_0\tau(0,t)\xi^2(z)} \tag{3.16}$$

For a specified s_0 and a target at distance z, F_0 is then the limit due to self-defocusing on the flux which can be transmitted through the atmosphere.

It is desirable to simplify (3.16) somewhat by going back to the definitions (3.10) of $\xi(z)$ and (2.18) of $T(z,t)$ and noting that

$$\xi(z) = \frac{1}{\sqrt{k_0\tau(0,t)}} \int_0^z \left[k(z'\cos\phi)\tau(z',t)\right]^{\frac{1}{2}} dz' \quad . \tag{3.17}$$

The term $k_0\tau(0,t)$ in (3.16) may be canceled and we obtain finally

$$F_0 = \frac{\gamma P s_0^2}{(\gamma-1)(n_a-1)\eta^2(z)} \quad . \tag{3.18a}$$

where

$$\eta(z) = \int_0^z \left[k(z'\cos\phi)\tau(z',t)\right]^{\frac{1}{2}} dz' \quad . \tag{3.18b}$$

Before we can obtain numbers from (3.18) we must still choose a function $\tau(z,t)$ which describes the beam rotation, and we must pick a value of s_0. In the next section we shall give several illustrative examples of the use of (3.18). In all of these examples we shall assume that the beam has lost its destructive ability when the beam edge has eaten its way in by one quarter of its original diameter, $s_0 = D/4$.

4. ILLUSTRATIVE EXAMPLES

In this section we shall treat several special cases so as to illustrate the use of (3.18) in calculating F_0, the flux limit due to self-defocusing. We shall assume we are using a CO_2 cw laser.* We mentioned in Section 2 that the altitude dependence of the absorption coefficient for CO_2 is rather complicated and uncertain. We shall simply assume that for our purposes it may be adequately represented by the altitude dependence of the atmospheric density,

$$k(z\cos\phi) = k_0 \, e^{-(z/L)\cos\phi} \quad , \tag{4.1}$$

where L is the atmospheric scale height, L = 8 km; the value of k_0 is $k_0 = 3\times10^{-7}\text{cm}^{-1}$. The values of the other constants which appear in (3.18) are as follows: The ratio of specific heats in air is $\gamma = 1.4$, the atmospheric pressure is $P = 10^6$ dynes/cm^2, and the ambient refractive index is $n_a - 1 \approx 3\times10^{-4}$. Also, in our examples we shall take the initial beam diameter to be D = 1m.

Case 1. Stationary Target

For a stationary target each air mass is illuminated for the entire laser pulse length t, so that we have

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* It is worth recalling here that, as was pointed out in Section 2, there is essentially no self-defocusing problem for giant pulse lasers; the density change requires a finite amount of time, which is of the order of milliseconds for a beam of 1 meter diameter. The current giant pulse laser is, however, not the answer to the self-defocusing problem, since the amount of energy that can be put out in one pulse is in general far too small for most applications. If we think in terms of a rapid succession of giant pulses, then we are in effect back to the cw laser.

$$\tau(z,t) = t \quad . \tag{4.2}$$

Using (4.2) and (4.1) to obtain $n(z)$, and taking $s_0 = D/4$, where D is the beam's initial diameter, we immediately find from (3.18),

$$F_0 t = \frac{\gamma P D^2 \cos^2\phi}{64(\gamma-1)(n_a-1)k_0 L^2 [1-\exp(-z\cos\phi/2L)]^2} \quad . \tag{4.3}$$

Note that the limitation here is not on the flux F_0, but rather on the total energy per unit area $F_0 t$ which can be transmitted.

If we consider the case of a target in the zenith direction ($\phi = 0$) at an altitude much greater than the atmospheric scale height ($z >> L$), then (4.3) simplifies to

$$F_0 t = \frac{\gamma P D^2}{64(\gamma-1)(n_a-1)k_0 L^2} \quad . \tag{4.4}$$

Putting in the numbers specified above we obtain

$$F_0 t = .95 \text{ joules/cm}^2.$$

Now let us consider the case in which both the target and the laser are on the ground, so that $\cos\phi = 0$. In this case (4.3) reduces to

$$F_0 t = \frac{\gamma P D^2}{16(\gamma-1)(n_a-1)k_0 z^2} \quad . \tag{4.5}$$

For a target at a distance of $z = 1$ km, (4.5) yields

$$F_0 t = 240 \text{ joules/cm}^2.$$

Case 2. Moving Target

For a moving target the accuracy of our results depends on how judiciously we choose the expression for $\tau(z,t)$, the mean illumination time of an air mass at distance z from the laser. If the angular coordinate θ of the target is changing at the rate $\dot{\theta}$, then at large distances z from the laser the beam is moving with a linear velocity $\dot{\theta}z$, so that the time taken for the beam to cross the air mass is

$$\tau(z,t) = D/\dot{\theta}z \quad . \tag{4.6}$$

At small distances this expression is quite invalid. The concept of an average illumination time is meaningful only if this time is less than the total pulse time, that is, if $\tau(z,t) < t$. However, the above expression for τ blows up at small z, so the required inequality is clearly violated If, nevertheless, we insert (4.6) into the expression (3.18b) for $n(z)$ to obtain

$$n(z) = \left(\frac{k_0 D}{\dot{\theta}}\right)^{\frac{1}{2}} \int_0^z \frac{e^{-(z'/2L)\cos\phi}}{\sqrt{z'}}\, dz' \quad , \tag{4.7}$$

we may note that for small z' the integral goes like $\sqrt{z'}$; consequently, the contribution to the integral is small from the range in which (4.6) overestimates the average illumination time.

We shall use (4.7), but first let us digress momentarily to get a crude, but somewhat more quantitative estimate of the error involved. For simplicity we take $\cos\phi \to 0$, so that the exponential in the integral becomes unity and the integral is directly evaluable. Then if we regard (4.6) as invalid up to a distance z_0, but valid for all larger distances, the

fractional error is immediately seen to be ... Now, z_0 is the distance at which τ becomes as large as t, so that from (4.6) we have $z_0 = D/\dot{\theta}t$. However, from (4.6) we also find that $D/\dot{\theta} = z$ ... $t)$. Therefore, the fractional error may be estimated to be $\sqrt{z_0/z} = \sqrt{\tau(z,t)/}$ ... We conclude then, that if the total pulse time t is sufficiently greater than the average illumination time $\tau(z,t)$ at the target, we may use (4.7).

Returning to (4.7) we obtain, after a simple transformation on the integral,

$$\eta(z) = \left(\frac{2\pi L k_0 D}{\dot{\theta}\cos\phi}\right)^{\frac{1}{2}} E(\sqrt{z\cos} \quad) \quad , \qquad (4$$

where

$$E(x) = \frac{1}{\sqrt{2\pi}}\int_{-x}^{x} e^{-t^2/2} \qquad (4.$$

is the normal probability integral, having the property $E(\infty) = 1$. Now from (3.18a) we obtain the desired expression for the limiting flux,

$$F_0 = \frac{\pi P D\dot{\theta}\cos\phi}{32\pi(\ -1)(n_a-1)k_0 L E^2\left(\sqrt{z\cos} \quad \right)} \qquad (4.$$

If the target is flying directly overhead we have $\cos\phi = 1$ and $\dot{\theta} = v/$ so that (4.10) becomes

$$F_0 = \frac{\pi P D v}{32\pi(\ -1)(n_a-1)k_0 L z\, E^2\left(\sqrt{z}\right.} \qquad (4.$$

Let us assume that the target is at an altitude $z = 10$ km and has a velocity $v = 500$ mph $= 2.23 \times 10^4$ cm/sec. We have assumed a subsonic velocity (sound velocity in air is 3×10^4 cm/sec), since, as we discussed earlier, our model is not applicable to supersonic velocities. For the chosen altitude and velocity we find from (4.11)

$$F_o = 197 \text{ watts/cm}^2.$$

The average illumination time of an air mass in the neighborhood of the target is $\tau = D/v = 4.5 \times 10^{-3}$ sec, so this result for F_o is meaningful only if the total laser pulse time length t is considerably greater than several millisec. For laser pulses shorter than $\tau = D/$ one would be more accurate in regarding the beam as stationary and using (4.3).

If the target is on the ground and moving normal to the line of sight with velocity v, we again have $\dot{\theta} = v/z$, but this time $\cos\phi = 0$, so that (4.10) reduces to (since $E(x) \cong \sqrt{2/\pi}\, x$ for $x << 1$)

$$F_o = \frac{\gamma P D v}{64(\gamma-1)(n_a-1)k_o z^2} . \qquad (4.12)$$

Taking a target velocity $v = 10$ m/sec ($= 21.6$ mph) and a target distance $z = 1$ km, we find

$$F_o = 610 \text{ watts/cm}^2.$$

In this case the average illumination time of an air mass near the target is $\tau = D/v = 10^{-1}$ sec, so that the laser pulse length must be somewhat greater than 10^{-1} sec for our model to apply.

APPENDIX

The equation to be solved is

$$\frac{\partial^2 X_1}{\partial \xi^2} - \frac{\partial^2 X_1}{\partial p^2} + \frac{df}{ds} = 0 \ , \tag{A1}$$

where X_1 (p,ξ) is the ray displacement,

$$X_1(p,\xi) = x_1(s,z) \ , \tag{A2}$$

and the (p,ξ) coordinate system is related to the (s,z) coordinate system by the transformations

$$\frac{dp}{ds} = \frac{1}{\sqrt{f(s)}} \ , \tag{A3}$$

$$\frac{d\xi}{dz} = \sqrt{T(z)} \ . \tag{A4}$$

The boundary conditions are that the initial displacement is zero,

$$x_1(s,0) = 0 \ , \tag{A5}$$

and the initial angle of any ray relative to the z axis is zero,

$$\theta(s,0) = \frac{\partial x_1}{\partial z}(s,0) = 0 \ . \tag{A6}$$

Now we define the functions $S(p)$, $P(s)$ and $\xi(z)$ by

$$p = \int_0^{S(p)} \frac{ds'}{\sqrt{f(s')}} , \tag{A7}$$

$$P(s) = \int_0^{s} \frac{ds'}{\sqrt{f(s')}} , \tag{A8}$$

$$\xi(z) = \int_0^{z} \sqrt{T(z')}\, dz' . \tag{A9}$$

According to (A3) the s-p transformation and its inverse are then given by

$$s = S(p) , \qquad p = P(s) . \tag{A10}$$

It will be seen shortly that defining the functions $S(p)$ and $P(s)$ is useful for avoiding notational confusion.

Next we transform the last term in (A1) as follows, using (A3) and (A10),

$$\frac{df}{ds} = \frac{dp}{ds}\frac{d}{dp} f[S(p)] = \frac{1}{\sqrt{f}}\frac{df}{dp} = 2\frac{d\sqrt{f}}{dp}$$

$$= 2\frac{d}{dp}\frac{ds}{dp} = 2\frac{d^2S(p)}{dp^2} , \tag{A11}$$

so that (A1) becomes

$$\frac{\partial^2 X_1}{\partial \xi^2} - \frac{\partial^2 X_1}{\partial p^2} + 2\frac{d^2S}{dp^2} = 0 , \tag{A12}$$

or

$$\left(\frac{\partial^2}{\partial\xi^2} - \frac{\partial^2}{\partial p^2}\right)(X_1 - 2S) = 0 \quad . \tag{A13}$$

The general solution of (A13) is well known to be

$$X_1(p,\xi) - 2S(p) = A(p+\xi) + B(p-\xi) \quad , \tag{A14}$$

where A and B are arbitrary functions.

Now we evaluate A and B from the boundary conditions (A5) and (A6). Since at $z = 0$ we have $\xi = 0$, it follows from (A5) that

$$X_1(p,0) = 2S(p) - A(p) + B(p) = 0 \quad , \tag{A15}$$

so that

$$B(p) = -2S(p) - A(p) \quad . \tag{A16}$$

We may now write (A14) as

$$X_1(p,\xi) = 2S(p) + A(p+\xi) - 2S(p-\xi) - A(p-\xi) \quad . \tag{A17}$$

To apply the second boundary condition (A6) we use the transformation (A4),

$$\frac{1}{\sqrt{f}} \frac{\partial x_1}{\partial z} = \frac{\partial X_1}{\partial \xi} = A'(p+\xi) + A'(p-\xi) + 2S'(p-\xi) \quad . \tag{A18}$$

Then from (A6) we obtain

$$2A'(p) + 2S'(p) = 0 \quad , \tag{A19}$$

or

$$A(p) = -S(p) + c \quad , \tag{A20}$$

where c is an arbitrary constant. Inserting this result into (A15) we now have

$$X_1(p,\xi) = 2S(p) - S(p+\xi)-S(p-\xi) \quad , \tag{A21}$$

The final task is to transform back to the (s,z) coordinate system. From the transformations (A7,8,9) we have

$$\dot{x}_1(s,z) = 2s-S[P(s)+\xi(z)]-S[P(s)-\xi(z)] \quad . \tag{A22}$$

In addition we have

$$P(s)+\xi(z) = \int_0^s \frac{ds'}{\sqrt{f(s')}} + \xi(z) \quad , \tag{A23}$$

$$P(s)+\xi(z) = \int_0^{S[P(s)+\xi(z)]} \frac{ds'}{\sqrt{f(s')}} \quad . \tag{A24}$$

Subtracting (A24) from (A23) yields

$$\xi(z) = \int_s^{S[P(s)+\xi(z)]} \frac{ds'}{\sqrt{f(s')}} \quad , \tag{A25}$$

which directly determines the function $S[P(s)+\xi(z)]$. Finally, we simplify the notation by defining the function $g[s,\xi(z)]$ as follows,

$$g(s,\xi) \equiv S[P(s)+\xi(z)] \quad . \tag{A26}$$

The solution may now be written in the (s,z) coordinate system as

$$x_1(s,z) = 2s-g(s,\xi)-g(s-\xi) \quad , \tag{A27}$$

where g(s,) is determined from

$$\xi = \int_s^{g(s,\xi)} \frac{ds'}{\sqrt{f(s')}} \quad , \tag{A28}$$

and $\xi(z)$ is defined as a function of z by

$$\xi(z) = \int_0^z \sqrt{T(z')}\ dz' \quad . \tag{A29}$$

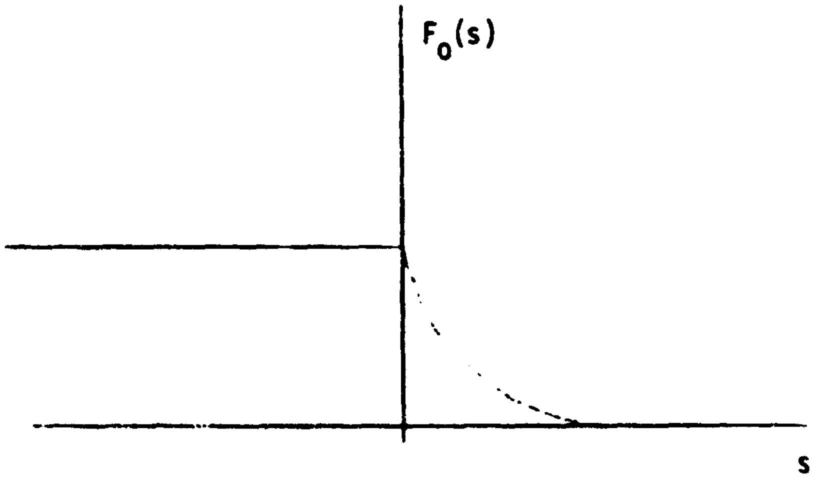

Fig. 1. Uniform distribution of flux $F_0(s)$ emanating from a semi-infinite laser face ($s < 0$), with an exponential fall-off at the edge. The rays originating in the uniform region along the negative s-axis are initially undeflected. Those originating along the positive s-axis are immediately deflected to the right.

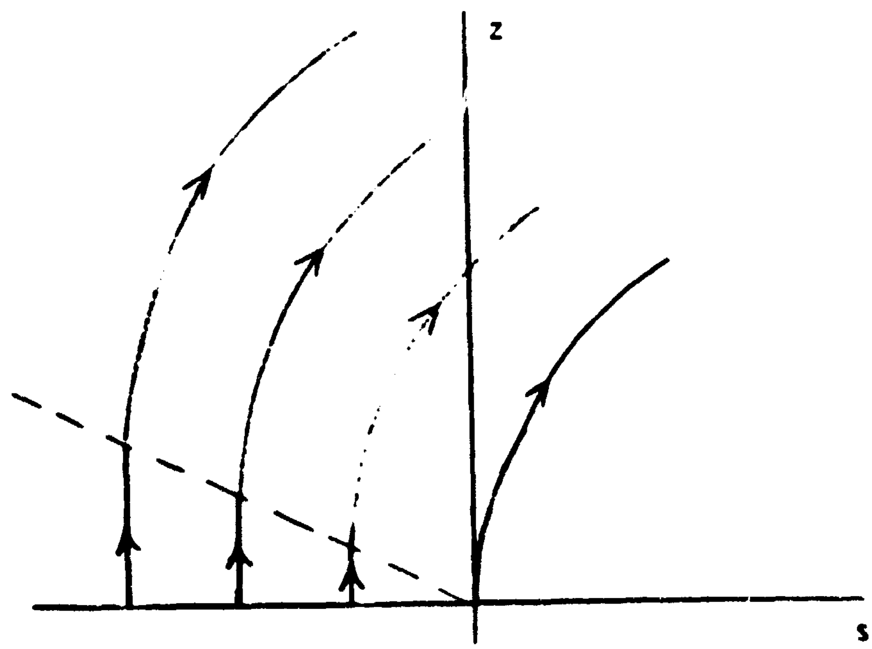

Fig. 2. Trajectories of rays emanating from the region of uniform flux distribution (s < 0) depicted in Fig. 1. The rays go out vertically until they intersect the dashed line, then they begin deflecting to the right parabolically with distance z.

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13. ABSTRACT

The research reported here involves the thermal self-defocusing effect, which occurs in the case of high energy laser beam propagation in the atmosphere. Two subjects are investigated, namely, heating mechanisms, and the dynamics of the propagating laser beam. The heating mechanism study is concerned specifically with photo-absorption in the far wings of pressure broadened CO_2 vibration-rotation bands, while the beam dynamics analysis treats the effects of target motion on the degree of self-defocusing of the laser beam. A theory of far-wing pressure broadening is developed in which the basic broadening mechanism is assumed to arise from perturbations of the absorber's rotational motion via a short range repulsive interaction with a colliding molecule. The theory predicts a far-wing spectral behavior described by a product of a Lorentz line shape and an exponentially decreasing factor, in general agreement with recent measurements. In the beam dynamics work a convenient closed form expression has been obtained for the maximum flux which the thermal self-defocusing effect permits one to transmit through the atmosphere. This analysis takes into account the effect of target motion. The expression for the maximum flux depends upon such parameters as the initial beam intensity, the initial beam diameter, the target distance, the rotational rate of the beam, and the effective absorption coefficient for heating of air by light at the laser frequency.

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